UNDERSTANDING THE SELECTIVITY, MECHANISM AND DYNAMIC EFFECTS INVOLVED IN SIMPLE ORGANIC REACTIONS

A Dissertation

by

YEXENIA E. NIEVES

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Chair of Committee,	Daniel A. Singleton
Committee Members,	David E. Bergbreiter
	Simon North
	Perla Balbuena
Head of Department,	Simon North

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ABSTRACT

Statistical models, like Transition State Theory (TST), are used in order to predict rates and selectivities of reactions. However, these models often fail to explain experimental results. In such cases, consideration of non-statistical dynamic effects is necessary to understand the experimental observations. Here, we present the study of a series of organic reactions, including: the nitration of toluene using nitronium salts, the Friedel-Crafts acylation of aromatic ethers, the Cope-type hydroamination of alkynes, and Diels-Alder cycloadditions. In order to understand the mechanism and dynamic effects involved in these reactions, a combination of experimental kinetic isotope effects (KIEs) and computational chemistry were employed. KIEs were determined using 1D ^{13}C NMR.

Solvent dynamics play a very important role in the product selectivity of the nitration of toluene. For this reaction, computational studies showed that the experimentally observed product selectivity does not involve any transition states. Also, dynamic trajectories using an implicit solvent model fail to account for the experimental product selectivity. However, the use of an explicit solvent model showed the importance of the solvent and counter ion reorganization, and their impact in the reaction's selectivity.

For the Friedel-Crafts acylation of aromatic ethers, KIEs showed that they are affected by a bifurcating energy surface. In these reactions we found that the first step,

formation of a C – C bond, is the rate-limiting step. However, KIEs showed that this step is affected by a bifurcation on the free energy surface. Computational studies were able to explain the experimental results.

The hydroamination of alkynes was studied in order to get a better understanding of the mechanism involved in this process. KIEs and computational results were in agreement with a process that occurs via a 5-membered-ring TS. In addition, the results showed how KIEs can give an accurate description of the TS involved in the process.

Finally, KIEs obtained for the Diels-Alder cycloaddition of *p*-chlorobenzaldehyde with an asymmetric silyl-diene showed the possibility of the reaction proceeding via a two-step process on the free energy surface, but as "seemingly concerted" reaction in potential energy. These results imply that the reaction is affected by non-statistical recrossing.

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NOMENCLATURE

TST	Transition State Theory
VTST	Variational Transition State Theory
TS	Transition State
IVR	Intramolecular Vibrational Energy Redistribution
MEP	Minimum Energy Path
KIE	Kinetic Isotope Effect
ZPE	Zero Point Energy
NMR	Nuclear Magnetic Resonance
VTS	Variational Transition State

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CHAPTER I

INTRODUCTION

Understanding the selectivity and rate of a reaction is of great importance in chemistry. Organic reactions are usually complex, and a mixture of products is obtained. Avoiding the formation of side products has always been a very important challenge for synthetic organic chemists. However, in order to be able to accomplish this, it is necessary to have insight on the underlying mechanism of the reaction. This is one of the reasons why the elucidation and understanding of reaction mechanisms is one of the main goals of physical organic chemistry.

The study of reaction mechanisms requires carefully designed experiments, such as: isotopic labeling, kinetic studies, crossover experiments, substituent effects, solvent effects, and the use of trapping agents to identify intermediates.[1-14] However, these experimental studies usually fail to probe complex systems and provide only a qualitative overview of a reaction's mechanism.[15] The development of computational and quantum chemistry has allowed chemists to use transition state theory (TST) and its derivatives, such as variational TST (VTST), to model organic reactions. This helps us to quantitatively understand and predict the reactivity and selectivity of a reaction.[16-17] However, theoretical studies can fail to account for the observed experimental results.[18] The limitations presented by experiments and computational chemistry can be overcome by developing studies that combine both methods in order to understand a reaction mechanism, product selectivity and rate of the reaction.

Dynamic Effects

TST is considered the most important statistical model used to understand the selectivity and rates of chemical reactions. A transition state (TS) is often thought as a particular geometry that must be passed through in order to get from reactants to products; however a more formal definition for this geometry is to consider it as a multidimensional surface that separates reactants from products. TST assumes that the rate of the process of going from reactants to products is governed by the relative energy of the transition state versus the reactants at thermal equilibrium. Even though this model has proven highly successful, it has limitations. There are many experimental observations, e.g. rate and selectivity, that cannot be explained or predicted by TST. Such observations will be referred to as dynamic effects.

TST simplifies the understanding of chemistry by allowing the rates and selectivity of reactions to be simply predicted from the properties of the TS. The "dynamic" part of dynamic effects refers to Newtonian dynamics. That is, when TST fails, one must fall back on the difficult but ultimately determinative consideration of the motions and momenta of atoms.[19-23] The main goal of our research group is to identify reactions where TST fails to account for the experimental observations and develop an understanding of the dynamic effects involved in these reactions.

One of the firsts examples of dynamic effects in an organic reaction involved the unusual stereochemistry of the rearrangement of vinylcyclopropane to cyclopentene. Using labeled reactant, it was found that this reaction proceeds via an unequal mixture of four stereochemical pathways. In this case, efforts for trying to explain the selectivity of

the reaction using TST failed. However, Doubleday found that the trajectories associated with the transition state of the rearrangement could fully account for the selectivity.[24-25] This dynamic effect is an example of the class of reactions that Carpenter has described as involving *dynamic matching*. TST assumes that the energy of the transition states for a multistep process is statistically distributed. This requires the intramolecular energy redistribution (IVR) to be faster than overcoming the barriers for subsequent steps. In the vinylcyclopropane case, the reaction involves an intermediate that is so short lived that IVR cannot compete. Because of this, the selection of the subsequent transition state path is the result of the energy been in specific modes that favor particular transition states over others that are exactly equivalent in energy.

A second class of dynamic effects is *non-statistical recrossing*. In this kind of dynamic effect the continuation of the motion of the atoms through an initial TS leads to a potential energy wall that reflects the trajectories back to the reactants. From the beginning of TST, it was recognized that recrossing happens, and recrossing is built into TST in the transmission coefficient. Modern versions of TST, e.g. variational transition state theory (VTST), are designed to minimize the effect of recrossing that occurs statistically. However, recrossing can occur that is not statistically predictable, and it can affect the selectivity of the process.[19, 26] An example of this dynamic effect was presented by Singleton for the [2+2]-cycloaddition of dichloroketene with *cis*-2-butene.[19] For this reaction, experimental results were explained by this phenomenon.

A third class of dynamics effect occurs on *bifurcating energy surfaces*. In general, TST assumes that the formation of different products from the same starting

material is the result of differing TSs. The relative ratio of the products will depend on the difference in energy of the TSs leading to each product. However, there are times in which only one TS is involved in the formation of both products.[14] Figure 1 – 1 shows two different kinds of energy surfaces in which this can happen. In Figure 1 – 1 (a), the potential energy surface is symmetrical and the minimum-energy path (MEP) *bifurcates* at a second transition state leading to two equivalent products. In case of Figure 1 – 1 (b), the energy surface is unsymmetrical and the MEP will only form a single product, so there is no bifurcation of the MEP. However, trajectories could lead to the formation of a second product. For this case, since there is no transition state associated with the trajectories partitioning between the formation of two products, TST cannot account for the observed product ratio. The term *bifurcating energy surface* refers to the fact that the surface allows trajectories to proceed in two ways.

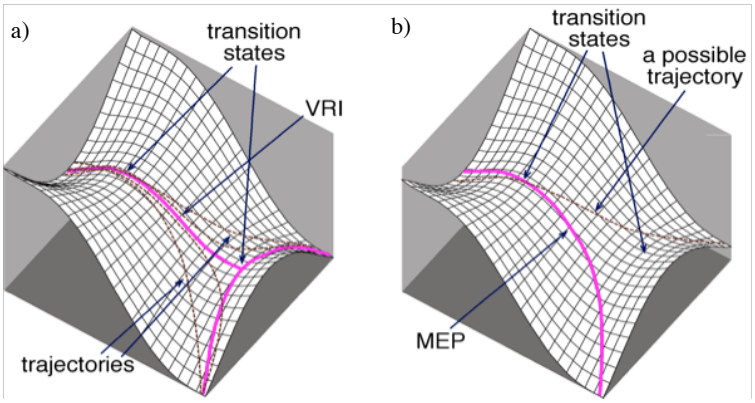

Figure 1 - 1: Symmetrical and unsymmetrical potential energy surfaces.

Another class of dynamic effects arises when there is *incomplete intramolecular vibrational energy redistribution*. An example of this phenomenon was reported by Oyola and Singleton for the hydroboration of terminal alkenes.[22] The hydroboration of terminal alkenes, followed by oxidation forms a mixture of primary and secondary alcohols. However, TST predicts that the amount obtained of the secondary alcohol should be negligible. In this article, they were able to explain that the ratio of products obtained was due to the reactivity of the intermediate π-complex. In this case, the π-complex reacts faster that the thermal equilibration of the molecule, affecting in this way the selectivity of the process. This is what we refer to as incomplete IVR. Another example of this dynamic effect was reported by Quijano and Singleton, for the ozonolysis of vinyl ethers.[23] We should define the distinction between this class of dynamic effects and those involving *dynamic matching*. In *dynamic matching*, specific motions in an intermediate, arising from the formation of that intermediate, lead to a specific selectivity among subsequent reactions. In *incomplete IVR*, the excess energy in an intermediate is simply localized in a part of the molecule, i.e. that part is "hot," without any particular product being favored.

In addition to these dynamic effects, we recently found that not only the reactive species can affect the rate, mechanism or selectivity of a reaction; but also, the solvent used can cause a change of these characteristics in a determined reaction. In our lab, we recently reported results for a Wittig reaction in which we discussed the possibility that the solvent can stabilize an intermediate enough to change the mechanistic pathway of the reaction.[18] With the results obtained we concluded that an intermediate for a

determined reaction would only exists if the solvent can stabilize it enough. We referred to this phenomenon as *solvent dynamics*. A similar result was observed for the nitration of toluene, as will be discussed in the next chapter.

In general, dynamic effects are phenomena that can affect the selectivity, rate and mechanistic path taken by a reaction to the determined products. In order to understand this processes we use a combination of experimental kinetic isotope effects (KIEs) and computational chemistry.

Kinetic Isotope Effects

KIEs are considered one of the most important observations when trying to explain a reaction's mechanism, because they provide structural information about the transition state for a determined reaction.[19-23, 27-35] This observation shows that substitution of an isotope in a molecule can lead to a change in the reaction's rate. The results obtained from KIEs can be classified in two categories: primary or secondary isotope effects. A primary kinetic isotope effect refers to the change in the reaction rate when the substituted isotope is directly involved in the rate-limiting bond changing process; it usually shows a big change on the rate.[36-38] On the other hand, if the atom is not involved in the rate-limiting bond changing process, but close to this atom, it will result in a small change in the rate of the reaction and will be considered as a secondary isotope effect.[39-40] Since KIEs are closely related to the bond changing process in organic reactions, they could be used as excellent probes to study reaction mechanisms. Isotopic substitutions that are far away from the reacting center have negligible influence

on the rate of a reaction, and for this reason, can be used as a standard when comparing the rate changes in isotopomeric reactions. In addition, isotopic substitution on the media of a reaction (solvent) can also lead to a change in rate. This kind of isotopic rate change leads to a solvent KIE, which are widely used in studying reaction mechanisms.

The KIEs for a determined reaction derive from the difference in the vibrational frequencies of the vibrational modes associated with the bond changing process of different isotopomers. For a given vibrational mode, the zero-point energy (ZPE) of the different isotopomers will be different (lower for the heavier isotope) (Figure 1 – 2). However, the difference in the ZPE between two isotopomeric vibrational modes depends on the shape of their potential energy well. In a tighter potential energy well (reactant or intermediate) the energy difference between the two isotopomers is bigger than those in a loose potential energy well (usually transition state). Based on this, it is possible to say, qualitatively, that the energy difference between reactants and transition state is larger for heavier isotopomers (Δ ZPE (^{H}X)), resulting in a slower reaction compared to the lighter isotopomer (Δ ZPE (^{L}X)).

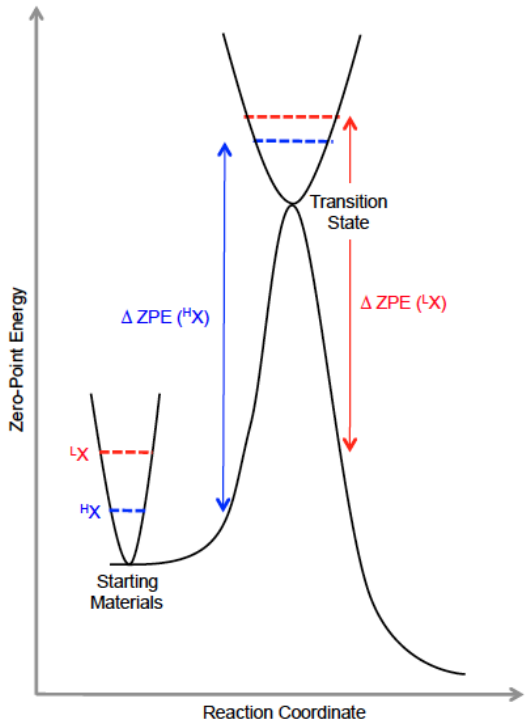

Figure 1 - 2: Zero-point energy of vibrational modes for isotopomers

The most used KIEs to study organic reactions are ^{2}H and ^{13}C. In general, KIEs are obtained by measuring the rate difference of these isotopomers in a determined reaction. These rates can be measured by various methods. Traditionally, KIEs have been measured by synthesizing labeled compounds. However, the synthesis of label materials is usually very challenging and expensive. Making the measurement of KIEs impractical for many reactions, especially when multiple positions are under study.

In order to overcome these limitations, Singleton developed a general methodology for the determination of KIEs at multiple positions in a molecule, at natural abundance, using Nuclear Magnetic Resonance (NMR) spectroscopy.[34] This method

takes the advantage of the inherent competition of the isotopologues at their natural abundance. The methodology can be applied for the measurement of intermolecular KIEs on starting material or product, and intramolecular KIEs. All the reported KIEs in this dissertation were obtained using the Singleton method.

Intermolecular KIEs can be defined as the measure of the impact of isotopic substitution on the overall reactivity of a molecule, and reflects the transition state for the rate-limiting step of a reaction. Starting material intermolecular KIEs are measured on recovered unreacted starting material from a reaction mixture. In this case, a reaction is taken to a high convertion (e.g. >70%), and the unreacted starting material is recovered from the reaction. This unreacted starting material will be enriched with the slowest reacting isotope (heavier isotope). NMR measurements of the recovered material and material that was not submitted to the reaction conditions (referred to as a standard), following Singleton[34] standard procedure, allows us to compare their isotopic composition and calculate the KIE. The relative isotopic composition (R/R_0) at each position in the molecule can be determined by integration of each peak of the NMRs for the recovered material and the standard. The KIE can then be calculated from the relative isotopic composition (R/R_0) and the reaction conversion (F) using the following equation (1-1).

$$KIE_{SM} = \frac{\log(1-F)}{\log[(1-F)\times R/R_0]} \qquad (1\text{-}1)$$

In some cases, the recovery of the starting material from the reaction mixture is complicated, due to the low volatility, low stability of the compound or impurities that prevent the purification of the material. In these cases, it is possible to measure intermolecular KIEs on the product. In order to measure intermolecular KIEs on the product, a reaction is taken to a low convertion (~20%), and the product is isolated from the reaction mixture. In this case, the product is enriched with the isotopomer that reacts faster. In addition, another reaction is taken to a 100% conversion; the product is isolated from the reaction mixture, and used as the standard for determination of the KIEs. This is possible because since the conversion is quantitative, the product is expected to have the same isotopic composition present in the starting material. The relative isotopic compositions can then be measured by integration of the NMR peaks, as mention before. The KIEs are again determined by the relative isotopic compositions (R/R_0) and the reaction conversion (F) using the following equation (1-2).

$$KIE_{Product} = \frac{\log(1-F)}{\log(1-F\times R/R_0)} \qquad (1\text{-}2)$$

In other cases, when one of the starting materials is symmetrical, is possible to measure intramolecular KIEs. This kind of isotope effect is the measure of the relative rate of reaction of equivalent positions in the starting material. Intramolecular KIEs characterize the first irreversible step undertaken by an initially symmetrical molecule

after loosing symmetry on the path to the product, referred to as the product-determining step. This kind of isotope effect measures the relative isotopic composition between two atoms in a single molecule. For this reason, they do not require the measure of a standard sample. The intramolecular KIEs are calculated based on the ratio of the integrations for the positions of interest in the product. For example, suppose there are two carbons **a** and **b**, that are equivalent in the starting material but not on the product. If the isotopic abundance for each carbon in the product at **a** is R_a and at **b** is R_b, the intermolecular KIE at **a** is defined as shown in the following equation (1-3).

$$KIE_{Intramolecular} = \frac{R_b}{R_a} \qquad (1\text{-}3)$$

A quantitative description of KIEs was proposed by Bigeleisen and Mayer in 1947.[41] The equation for this description is shown below (1-4).

$$KIE_{TST} = \frac{v_1^{\ddagger}(s_2/s_1)f_{GS}}{v_2^{\ddagger}(s_2/s_1)f_{TS}} \qquad (1\text{-}4)$$

Where,

$$(s_2/s_1)f_{GS} = \prod_{i}^{3N-6} \frac{v_{2i}}{v_{1i}} \frac{1 - e^{-u_{1i}}}{1 - e^{-u_{2i}}} \frac{e^{u_{1i}/2}}{e^{u_{2i}/2}}$$

$$(s_2/s_1)f_{TS} = \prod_{i}^{3N-7} \frac{v_{2i}}{v_{1i}} \frac{1 - e^{-u_{1i}}}{1 - e^{-u_{2i}}} \frac{e^{u_{1i}/2}}{e^{u_{2i}/2}}$$

$$u_i = {}^{hv_i}/_{kT}$$

The equation takes in consideration three factors: temperature, the reduced isotopic partition function or fractional factor, and the frequency of the vibrational modes. This equation relies on conventional TST and the harmonic approximation, but it has been highly successful for the prediction of experimental KIEs when no significant tunneling is affecting the reaction.

Tunneling is defined as the quantum mechanical process by which a particle can traverse a barrier without having sufficient activation energy to cross it. This phenomenon can be associated with any of the vibrational modes of a molecule. However, a full allowance for tunneling in all the vibrational modes of a molecule is complicated, instead only the modes that are associated with the bond changing

processes are considered. The barrier for the process is then treated as an infinite parabola with the curvature of the parabola defined by theoretical calculations.

CHAPTER II

DYNAMICS AND THE REGIOCHEMISTRY OF NITRATION OF TOLUNE*

Introduction

Nitration of aromatic compounds was originally performed by using a mixture of acids. Euler, in 1903, was the first person to suggest that this reaction proceeded via the formation of a nitronium ion, which will then act as an electrophile to react with the aromatic ring. However, this specie was not established as the reactive electrophile until 1946.[42] Since then, new chemicals have been developed for the nitration of aromatic compounds. Nowadays, the most commonly used is nitronium tetrafluoroborate.[43-45] This chemical eliminated the step for the formation of the nitronium specie, increasing the rate of the reaction. Great many experiments have been done in order to try to understand the selectivity of this kind of reactions.[42-47] However, there are many observations that cannot be explained or rationalized yet.

In general, the results obtained from an experiment are initially explained within the available theories. However, conflict can arise when an observation does not fit with the standard interpretive ideas. In order to make these anomalies fit into the known

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theories, scientists usually suggest complications, allowing this way the anomalies to fit into the existing theory, and the remained inconsistencies are then ignored. An explanation for the observation can only arise with the development of new interpretative ideas. Here, we describe how this pattern applies to the understanding of the regiochemistry of nitration of toluene. We present evidence supporting a new mechanistic understanding of this reaction based on dynamics.

Over 50 years ago, Olah and coworkers reported very unusual results in the nitration of toluene with the highly reactive nitronium salts.[45, 47] The most important observation was that the *inter*molecular selectivity between toluene and benzene was low (less than a factor of two) while the *intra*molecular (positional) selectivity with toluene was high, forming only 3% of the *meta*-substituted product. These observations make the *meta*-positions seem less reactive than individual benzene positions. With these observations in hand, Olah proposed that the inter- and intramolecular selectivities were determined in separate steps (Figure 2 – 1), with intermolecular selectivity determined in rate-limiting formation of a π-complex (**1**) followed by positional selectivity determined in the formation of the σ-complex (**2**).

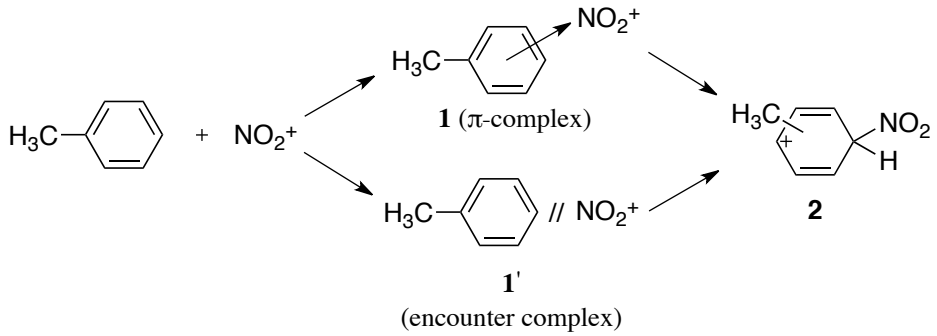


Figure 2 - 1: Possible mechanistic paths for nitration of toluene

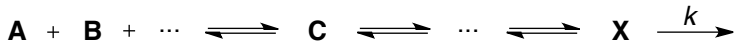
Olah's proposal was very controversial. The nature of the step determining the intermolecular selectivity was questioned. Ridd proposed that the reaction fallowed either macroscopic mixing or microscopic diffusional encounter.[48] This proposal was contested, because it failed to explain the importance of the π-complex in accounting for high selectivity, but considerable evidence supported encounter-controlled reactions in some nitrations.[49] On later discussions, Olah combined the π-complex **1** and encounter complex **1'**.[50] From a different perspective, it was argued that inter- and intramolecular selectivity anomalies were rare and of insufficient magnitude to require separated rate-determining and product-determining transition states (TSs).[51-52] However, no agreement was reached for this issue.[53]

The general nature of the mechanism for the reaction was contested. Other proposals, like electron transfer, have been discussed. The proposal for electron transfer been involved in this reaction has a long history in literature.[54-57] This mechanism was supported for reactions of highly electron-rich aromatics.[58-63] However, it was argued

that, for less electron-rich arenes, like toluene, the electron transfer process would be too slow to explain the observed rates of the reaction.[64-65] It is important to note that the reactivity of the arenes correlates well with the stability of σ-complexes through a broad scale that includes both, electron-rich and electron-poor aromatics.[66] Like Olah and many others, Kochi found the selectivity observed for the nitration of toluene to be an interesting point. Kochi proposed that the nearly constant selectivity for the nitration of toluene under different conditions required the formation of a common intermediate, which he suggested was supported by electron transfer.[60, 67]

Recently, a paper by Koleva *et al.* has claimed the observation of a benzene / NO_2^+ π-complex by direct UV-visible spectroscopy on the reaction under classical HNO_3 / H_2SO_4 conditions.[68] This would be a very important experimental observation; Kochi had observed many electron donor-acceptor complexes of arenes with molecular NO_2-X (X = OH, OAc, NO_3, Cl, pyr, $C(NO_3)_3$) species,[58-62, 67] in addition to NO_2^+ σ-complexes,[69] but Olah's NO_2^+ π-complexes had never been observed. However, there is reason to doubt that the observed absortion is due to a benzene / NO_2^+ π-complex. In any thermal reaction in which a mechanistic intermediate **X** is irreversibly converted to the product with a rate constant *k* (eq 1), the rate of the product formation will be defined by eq 2, and the concentration of **X** will follow eq 3 (as a maximum, assuming a single mechanistic pathway). Koleva's calculated barrier for product formation from the π-complex was 3-4 kcal/mol, making the rate constant ~10^{10} s^{-1}, and the observed rate was 3 x 10^{-5} M s^{-1}. This places the expected concentration of the π-complex from eq 3 at 3 x 10^{-15} M, a concentration that is at least nine orders of magnitude too low for the observed

absorbance of ~0.5. If we assume that the extinction coefficient of the π-complex is on the order of 100,00, the observed absorbance could only be obtained if the rate constant for reaction of the π-complex were 6 s^{-1}. This will require a barrier of 16.4 kcals/mol, over 12 kcals/mol higher than the low calculated barrier. Even ignoring the large computational discrepancy, a barrier of 16 kcal/mol for a highly exothermic simple bond formation in an ion-molecule complex would be unprecedented.



(1)

$$\text{rate} = k\,[\mathbf{X}] \qquad (2)$$

$$[\mathbf{X}] = \text{rate} / k \qquad (3)$$

Usually, one tends to associate the positional selectivity in the nitration of toluene with multiple TSs leading from an initial intermediate to the regioisomeric σ-complexes. All the mechanistic proposals agreed on this point. Until recently, chemistry did not have the concepts needed for an alternative explanation of the selectivity in the nitration of toluene. In this chapter we describe how the selectivity can arise without involving either intermediates or transition states. We also show that even when transition states are present, their energies cannot be used to understand the selectivity.

Results and Discussion

Here, we have reexamined the nitration of toluene by a combination of experimental and computational methods. Even though over a 100 different reaction conditions have been developed to achieve the nitration of arenes,[43] we chose to study nitrations using the stable nitronium tetrafluoroborate ($NO_2^+BF_4^-$) salt in dichloromethane (Figure 2 – 2). In general, almost all nitration conditions provide more *ortho*-nitrotoluene (**3a**) than *para*-nitrotoluene (**3c**), with 2-5% *meta*-nitrotoluene (**3b**). However, the choice of solvent and nitrating reagent has definite effects in the selectivity. It has been previously reported that nitrations using preformed nitronium salts in polar solvents such as nitromethane and tetramethylenesulfone tend to produce high **3a:3c** ratios (>1.75); however, nitrations done in chlorinated solvents or neat aromatic give lower **3a:3c** ratios of 1.2-1.6. In this case, the ratio of products we observed was typical for these conditions with diverse nitronium ion sources. The selectivity change was negligible over a concentration range varied by three orders of magnitude.

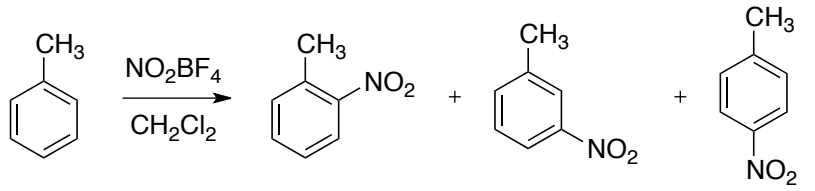


Figure 2 - 2: Nitration of toluene in dichloromethane using nitronium tetrafluoroborate

Computational method selection. Before starting to explore the solution reaction computationally, we did an extensive search for identifying a DFT method that would be both practical for broad study and energetically accurate on the gas-phase energy surface. After trying a wide range of DFT methods, none were completely satisfactory. Two main problems were encountered with DFT methods, and ultimately we found a way to address each one of them.

The first problem was that DFT methods tend to overestimate the electrophile affinity of aromatics. We found that for benzene, the proton affinity was overestimated by most methods, with exception of the M06-2X and M11 functionals; also, it was found that this overestimation was worst for the affinity of NO_2^+ to toluene. After this extensive functional study, we decided to use the M06-2X functional with a 6-311G* basis set because this combination had three attractive features: 1) It minimixed the overestimation of the electrophile affinity (as gauged by G3B3 and CCSD(T) energies) versus all other methods explored with the exception of M11/6-311G*; 2) It exhibited the lowest mean absolute deviation in the relative energies of NO_2^+ / toluene σ-complexes **2**, at 0.3 kcal/mol versus G3B3 energies; 3) The M06-2X/6-311G* energy profile for approach of NO_2^+ to toluene very closely matched CCSD(T)/aug-cc-pvdz energies for N – C interatomic distances between 2 and 3.2 Å. Since the reaction selectivity is decided in this range of the energy surface, we decided that the M06-2X/6-311G* surface would be adequate for the purpose of this reaction. The accuracy of this method's energies was determined again by comparison to CCSD(T)/aug-cc-pvdz

energies for a series of five toluene / NO_2^+ TSs (see below), and the relative energies agreed within 0.1 kcal/mol.

The second problem was that all the explored DFT methods greatly underestimated the stability of the BF_4^- toward fluoride transfer to NO_2^+, in comparison with CCSD(T)/jun-cc-pvtz calculations. The unreal decomposition of the $NO_2^+BF_4^-$ that was found in trajectories and in any gas-phase calculations is likely product of a well-known tendency for DFT to err in the energy of dative bonds.[70] This problem was addressed in two ways. Since solvent stabilization of charge leads to a barrier to the decomposition, it was possible to locate stationary points on an M06-2X/6-311G*/PCM(CH_2Cl_2) surface, and to carry out short trajectories on this surface. In addition, a full range of stationary points, trajectories, and potential mean force (PMF) calculations in explicit solvent were carried out on an ONIOM surface, using M06-2X/6-311G* for the toluene / NO_2^+ and PM3 for the BF_4^- (and CH_2Cl_2 molecules when explicit solvent was employed). On the ONIOM surface, the interaction of BF_4^- with NO_2^+ occurs purely in the PM3 layer, and the PM3 surface correctly disfavors fluoride transfer from BF_4^- to NO_2^+. This had the effect of avoiding the unrealistic $NO_2^+BF_4^-$ decomposition while accurately retaining the electrostatic effect of the counterion.

The multilevel failure of conventional computational studies in implicit solvent. In order to find both TSs and π-complex-like minima for the reaction of toluene with either NO_2^+ or $NO_2^+BF_4^-$, a semi-automated search algorithm was used. In this algorithm, classical trajectories were carried out at 25 ºC on a M06-2X/6-311G*/PCM(CH_2Cl_2) (for NO_2^+) or the ONIOM (for $NO_2^+BF_4^-$) surface with the

distance between the nitrogen atom and the nearest aromatic carbon constrained by a loose harmonic potential (set at 2.4 or 2.7 Å in the search for TSs and 3.0 Å in the search for π-complexes). In each case, over 150 from a series of independent trajectories were extracted and used as the starting points for optimizations. The optimized structures were then systematically varied with respect to the positional orientation were chosen using researcher intuition. However, in no case this lead to a new low-energy structure.

A total of five TSs and twelve π-complex structures were located for the addition of NO_2^+ to toluene in the M06-2X/6-311G*/PCM calculations. The addition of NO_2^+ to toluene is a very exothermic reaction (18-25 kcal/mol), and the calculated TSs for the addition are all quite "early". Three of the TSs are shown in Figure 2 – 3a. Surprisingly, the lowest energy TS is the one that leads to the *ipso* σ-complex by intrinsic reaction coordinate (IRC) analysis. Also, no TS lead to the *meta* σ-complex by the same IRC analysis. If the reactions product ratio was predicted by using the calculated TSs energies and IRC, the mixture of σ-complexes would be 26% *ipso*, 20% *ortho*, 0% *meta*, and 54% *para*. However, this approach is incorrect for this reaction because trajectories passing through each of the TSs can afford multiple products. For example, in **4a**‡ the NO_2^+ can attack three different positions in the aromatic ring (the *ipso* and either of the two *ortho* positions). This means that there is a *bifurcation* or *multifurcation* of the energy surface after each TS.[14, 19, 26, 71-73] Under special cases it is possible to obtain a statistical prediction of the selectivity of the reaction by using variational transition state theory (VTST) and the Lluch procedure,[19, 74-75] but attempts to locate the necessary separate variational TSs were unsuccessful here, as is often the case.[71] This makes

impossible a statistical prediction or understanding of the selectivity, and it is necessary the employment of the trajectory methods for a quantitative prediction.

Quasiclassical direct-dynamics trajectories were run using each of the five TSs as the starting point, M06-2X/6-311G*/PCM was used as the surface. Each normal mode in each structure was given its zero-point energy (ZPE) plus a randomized excitation energy based on a Boltzmann distribution, along with a randomized displacement of modes. After allowing for a Boltzmann weighting of the five TSs, including entropies of mixing versus the achiral **4a**‡, and allowing for the mixtures of isomeric products obtained from each TS (see Figure 2 – 3a), the predicted mixture of σ-complexes **2** would be 21% *ipso*, 20% *ortho*, 11% *meta*, and 48% *para*.

This is a very bad prediction in many ways. First, the *para* σ-complex is incorrectly predicted to exceed the *ortho* σ-complex. Second, the predicted amount of *meta* σ-complex is too high by a factor of five. Finally, based on literature results, the amount of *ipso* σ-complex is also far too high; literature reports say that only 3.1% *ipso* adduct is formed under conditions that capture the intermediate σ-complex.[76-77] Overall, even after allowing for trajectory outcomes on a multifurcating surface, the toluene / NO_2^+ / implicit solvent physical model is simply inadequate for predicting or understanding the selectivity.

When this approach failed to account for the selectivity of the reaction, we decided to include the BF_4^- in our model. After including the BF_4^-, a total of 38 TSs and 36 π-complex structures were located using the M06-2X/6-311G*/PCM (CH_2Cl_2) surface. This large number of structures aroused from the multiplicity of positions for

the BF_4^- ion. Three of the TSs are shown in Figure 2 – 3b (**5a**‡, **5b**‡, and **5c**‡). The results show that the six lowest-energy structures are all oriented for attack at the *ipso* carbon, as in **5a**‡ or the *ortho* carbon, as in **5b**‡. After locating all the TSs and π-complexes, each of the nine lowest-energy TSs were used as starting points for quasiclassical trajectories, following all the procedures employed above for the cationic system. As on the previous case, the IRCs are misleading, and trajectories derived from six of the nine TSs afford a mixture of products. After allowing for a Boltzmann weighting of the nine TSs and the mixture of σ-complexes obtained for each, the predicted mixture of σ-complexes **2** would be 78% *ipso*, 19% *ortho*, 0.1% *meta*, and 3% *para*. This poor prediction could be the result of a too-tight interaction of the NO_2^+ and BF_4^- ions, associated with the unreal fluoride-transfer decomposition process on DFT surfaces. The ONIOM surface described above avoids this problem.

Using an ONIOM(M06-2X:PM3)/PCM surface we were able to locate a total of 42 TSs and 102 π-complexes for the toluene / $NO_2^+BF_4^-$ reaction. The π-complex structures located have closest C – N interatomic distances of 2.7-2.9 Å and are located in extremely shallow minima, never more than 0.7 kcal/mol below the lowest-energy TSs. The sets of located TSs and π-complexes are misleading; there are no low-energy TSs for attack at the *ortho* or *ipso* positions because the stack has no potential-energy barrier with favorable positions of the BF_4^- counterion. As a result, the seemingly exhaustive search process is biased for TSs associated with barriers, with attack *para* or *meta* (e.g., **6a**‡ and **6b**‡) over those that face no barrier. In order to avoid this problem, we located canonical variational transition states (CVTSs), e.g. **6c**‡, for attack at the

ortho and *ipso* positions using Truhlar's no-saddle procedure.[78] Each of the low-energy TSs and CVTSs were then used as the starting point for quasiclassical trajectories as above. Twelve of the thirteen sets of trajectories afford mixtures of σ-complexes. Based on a Boltzmann weighting of trajectory outcomes from comparable TSs / CVTSs, the predicted mixture of σ-complexes **2** would be 12% *ipso*, 20% *ortho*, 27% *meta*, and 29% *para.* This selectivity is very low. This might be expected for these very early TSs, but it is clearly inconsistent with experiment.

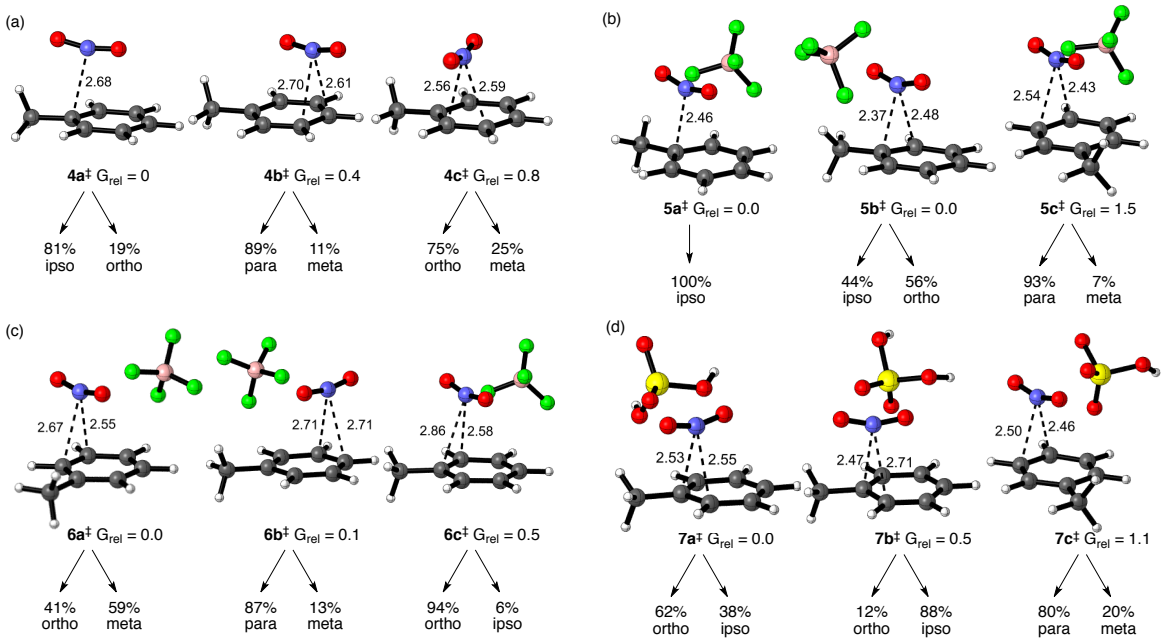


Figure 2 - 3: Example TSs for the nitration of toluene, along with the ratio of products obtained from quasiclassical trajectories passing through the structures. (a) NO_2^+ without a counterion, M06-2X/PCM(CH_2Cl_2). (b) $NO_2^+BF_4^-$, M06-2X/PCM(CH_2Cl_2). (c) $NO_2^+BF_4^-$, ONIOM/PCM(CH_2Cl_2). (d) NO_2^+ / H_2SO_4, M06-2X/ PCM(CH_2Cl_2).

One could argue that calculations in a polar sulfuric acid medium should be more successful, because the counterion effects should be minimized. As will be discussed later, there are also reasons to consider whether TSs are more relevant to the selectivity in sulfuric acid nitration's than in the $NO_2^+BF_4^-$ / CH_2Cl_2 system. For this reason, we explored the nitration of toluene with NO_2^+ including an additional sulfuric acid molecule in M06-2X/6-311G* calculations including a PCM model for sulfuric acid (following the general process of Koleva *et al*.[68]). A total of 28 TSs were located for the formation of the σ-complex in these calculations, but none of the TSs would afford *meta*-**2** by IRC. If only de energies of the TS by themselves were used to predict the selectivity, the percent ratio of products would have been 11% *ipso*, 76% *ortho*, 0% *meta*, and 13% *para*. As the previous predictions, these results are very poor.

Up to this point, all the attempts to understand the selectivity of the nitration of toluene based on TSs have failed on multiple ways. Predictions of the products ratios from the energies of TSs fail entirely to account for the experimental selectivity. On higher level, the implicit assumption that TSs lead to a single product, fails. Finally, even when the TS studies are combined with trajectory studies to allow for the mixture of products obtained from the various TSs, the calculations are still unable to provide a reasonable prediction of experimental observations.

When calculations employing only an implicit solvent models fail to account for the experimental observations, one might be tempted to attribute the results to inaccuracies in the potential energy surface. However, limitations of the physical model employed must be considered. One issue is that even a perfectly accurate potential

energy surface may be quite misleading in comparison to the decisive free-energy surface, and the accurate allowance for entropic effects in implicit solvent is a challenging problem.[79] A significant advantage of physical models including explicit solvent is that satisfactory methods exist to explore the solution free energy surface directly. A second issue is that implicit solvent models do not account for the dynamics of solvent motion and reorganization. As will be shown later, the same energy surface as employed above in combination with explicit solvent and a complete physical model including dynamics, can accurately predict and explain the experiment selectivity.

Even though the TSs do not account for the selectivity, there is a common structural feature that should be considered. It was observed that out of 115 TSs located, 105 of them showed that the nitronium ion is approaching the aromatic ring on a path that is approximately splitting two carbons. This behavior can be seen in all of the structures in Figure 2 – 3 except **4a**‡ and **5a**‡. This tendency to approach between two carbons aids the formation of multiple products from trajectories through the multiple TSs.

Potential mean force calculations in explicit solvent. In order to explore the free-energy surface and for dynamics including solvent motion, our computational model consisted of toluene and $NO_2^+BF_4^-$ in a sphere of 101 CH_2Cl_2 molecules with a diameter of 25.8 Å and density of 1.3. The model was explored on the QM/QM ONIOM surface, using M06-2X/6-311G* for the toluene / NO_2^+ and PM3 for the BF_4^- and CH_2Cl_2. First, we set out to determine the general shape of the free-energy surface as the $NO_2^+BF_4^-$ approaches the toluene by determining the potential of mean force (PMF) versus the

nitrogen – arene carbon distance using umbrella sampling. This process had the complication that biasing potentials based on individual C – N distances do not preclude attack of the NO_2^+ on alternative arene carbons. In order to avoid this complication, the biasing potential was based on the distance of nitrogen atom to six interlocking spheres centered on the arene ring carbons. This approach gave a PMF that represents a composite of the PMF for approach to the individual carbons, weighted by the equilibrium between the differing approaches.

The PMF profile was determined in both molecular dynamics (MD) and Monte Carlo calculations. A total of 1 ns of MD was obtained on the QM/QM surface, while the Monte Carlo surface is based on 400,000 successful steps (~ 30%) using an efficient ad hoc stepping algorithm. The PMF was then calculated by the weight histogram analysis method.[80] The results are shown if Figure 2 – 4.

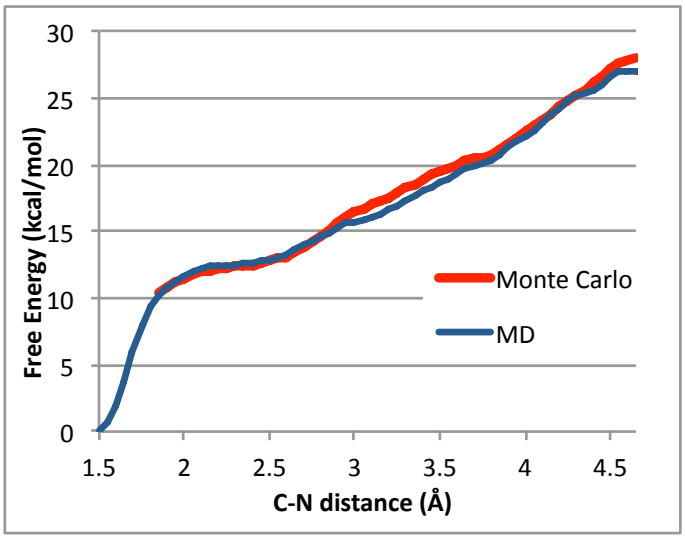


Figure 2 - 4: Potential of mean force curves for approach of $NO_2^+BF_4^-$ to toluene in a sphere of 101 CH_2Cl_2 molecules. The zero energy is the *para* isomer of 2, and the level of the limited Monte Carlo curve is set arbitrarily.

From this data, we noticed a striking observation. That is, *there is no free-energy barrier along the C – N distance coordinate*. We found that at any distance within 4.5 Å, approach of the $NO_2^+BF_4^-$ to the arene is favored and the system is has to form some isomer of **2**. In addition, the results showed that at equilibrium, **2** is >95% *para*. This preference for encounter complex over their diffusional separation is not surprising, as this is the expected behavior in the modern view of the mechanism. However, the apparent absence of TSs after formation of the encounter complex has never previously been suggested. This absence contradicts all the basic ideas presented in previous explanations of the selectivity.

We noted that the various TSs and π-complexes obtained with an implicit solvent model had no physical counterpart in explicit solvent. At a C – N distance range of 2.5 to

2.9 Å, where the TSs and π-complex structures were located in implicit solvent, the free-energy profile was steep. Implicit solvent calculations also showed similar overall energetics to those obtained from the PMF, but they show barriers of the potential energy curve in an area where there is no such feature on the free-energy surface.

Trajectories in explicit solvent. The selectivity of the exergonic slope was explored in trajectories using the explicit solvent model described before. The starting points for the trajectories were obtained from a series of independent simulations that were equilibrated at 25 ºC with the distance between the NO_2^+ nitrogen and the closest aromatic carbon constrained to ~3.4-4.0 Å using a loose biasing potential. At this distance range, the nearest carbon to the NO_2^+ was found to vary statistically. Structures and velocities were extracted from the equilibrated system at 250-fs intervals, and they were integrated forward and backward in time with no constraint. In none of these cases the NO_2^+ dissociated from the toluene, in keeping with the PMF curve. Instead, each trajectory resulted in the formation of one of the regioisomers of **2** (defines by a C – N distance of <1.6 Å). Even though most of the trajectories were stopped at the formation of the **2**, some trajectories were continued to see the behavior of the σ-complexes. It was found that, for trajectories affording the *ortho*, *meta* and *para* complexes, the highly acidic proton of the σ-complex was transfer from the nitrated center to either the BF_4^- or a solvent molecule to form the final product. In addition, no reversibility or rearrangement of the σ-complex was observed. This result supports the idea that the selectivity is determined kinetically in the formation of the σ-complexes.

Another interesting fact about our computational results was that the regiochemistry of the σ-complex formation was independent of the starting geometry of the trajectories. This can be seen from the absence of a correlation between the outcomes of the trajectories integrated forward and backward in time (46% of the pairs afforded the same product, compared to 45% expected from random distribution). A total of 672 trajectories were completed, and the results are summarized in Table 2 – 1.

Table 2 - 1: Experimental and Trajectory-Predicted Regioselectivity in the Nitration of Toluene.

	para	*meta*	*ortho*	*ipso*
Experimental	41%	2.0 ± 0.2%	57%	[a] 3.1 ± 0.7[b]
Trajectories with Toluene / $NO_2^+BF_4^-$ / CH_2Cl_2	304 (45% ± 2%)	15 (2.2% ± 0.6%)	330 (53% for *ortho* + *ipso* ± 2%)	23 (3.4% ± 0.7%)
Median Time (fs)	2754	3815	3332	4737
Equilibrium σ-complex mixture[c]	98%	0.01%	2%	0.002%

[a]*Ipso* attack is not measurable under our reaction conditions; the *ipso*-**2** is expected to rearrange or to *ortho*-**2** and afford the ortho product.[81] [b]For nitration in nitric acetic anhydride.[76-77] [c]From M06-2X/6-311G*/PCM free energies. The same trend is seen in G3B3 and CCSD(T) gas-phase energies.

Some very interesting observations were noticed from the trajectories. The most striking observation was that they take an impresive long time to afford the σ-complexes. The median time was 3100 fs. This can be compared to the median of only 75 fs taken in nitration trajectories that were started from transition structures **4**‡ – **7**‡ and

50 – 300 fs typically required to traverse the downhill slope in a cycloaddition. The median time required to afford *para*-**2** (Table 2 – 1) was interestingly shorter than that for other σ-complexes, with formation of *ipso*-**2** requiring a median of 4700 fs. It is important to point out that there are no interposing solvent molecules that could block the NO_2^+ attack. The NO_2^+ is often directly over a reactive aromatic carbon (Figure 2 – 5), appearing well-positioned for bond formation. Even so, product formation is over an order of magnitude slower than normally expected.

A second observation is that the product is not "decided", this is, it cannot be predicted from the position of the NO_2^+ relative to the toluene, until very late in the trajectory. As can be seen from the trajectories shown in Figure 2 – 5, the NO_2^+ roams the area above the plane of the aromatic carbons, avoiding the middle of the ring, moving from carbon to carbon. The closest carbon (based on the shortest C-N distance) changes a median of 27 times over the course of each trajectory. The final switch between closest carbons happens a median of 260 fs before the σ-complex forms, at a median C-N distance of 2.42 Å. Before this happens, the NO_2^+ can approach multiple aromatic carbons without forming a bond. Before the final approach of the NO_2^+ to the reacting carbon, about 85% of the trajectories have the NO_2^+ pass around 2.3 Å of a different carbon atom, and 25% of the trajectories have the NO_2^+ pass less than 2.0 Å from an ultimately non-reacting carbon. The NO_2^+ may also closely approach the reacting carbon then move away; 50% of the time that an NO_2^+ gets within 2.0 Å of a carbon, it later retreats to >2.3 Å.

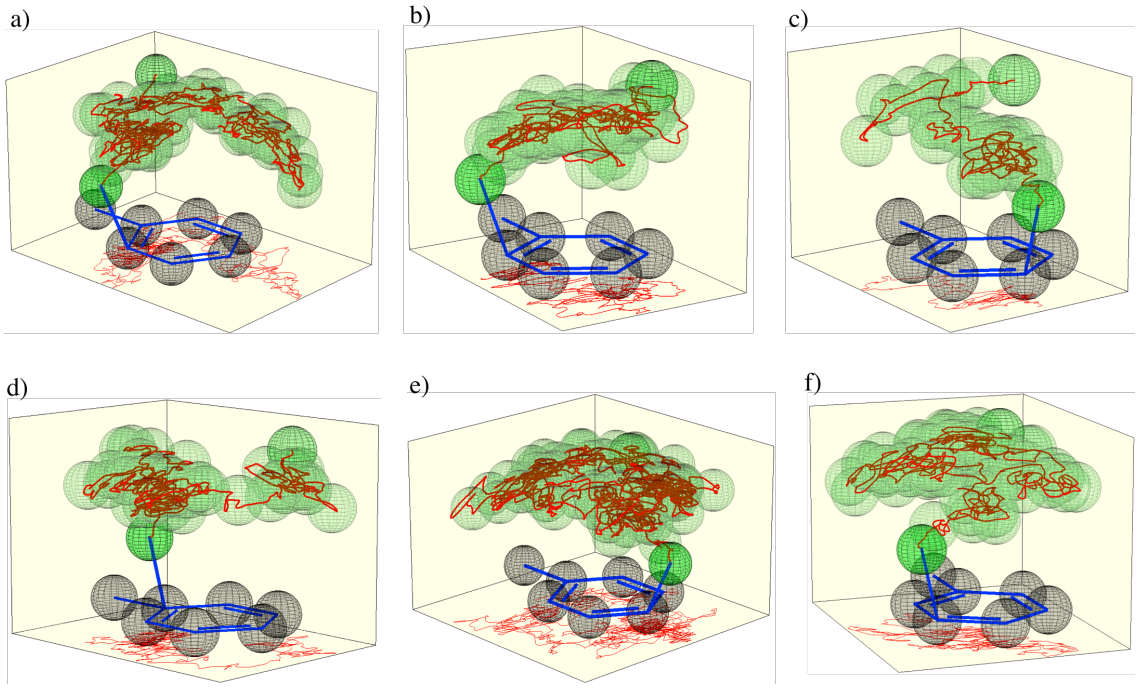


Figure 2 - 5: Motion of the nitrogen atom of $NO_2^+BF_4^-$ relative to the average position of the toluene carbons in trajectories in 101 CH_2Cl_2 molecules. The paths are depicted in red and transparent green spheres are added to clarify the 3-dimentional motion. A 2-dimenthional trace of the path is shown on the floor of the figures.

The most important observation is that the trajectory outcomes predict accurately the regioselectivity of this nitration (Table 2 – 1). In order to compare the computational results with the experimental observations, it is necessary to allow for the formation of *ipso*-**2**. The *ipso* attack in nitrations of alkylbenzenes is a well-known process. It was reported in literature that the *ipso* σ-complex can be trapped, and for the nitration of toluene in acetic anhydride it affords 3.1% ± 0.7% trapped *ipso* adduct.[76-77] This observation matches perfectly with the 3.4% *ipso*-**2** obtained from trajectories. Under our reaction conditions it is not possible to trap the *ipso*-**2**, and it would be expected to

undergo exclusively intramolecular 1,2-shift of the nitro group to afford the *ortho* product.[81-82] Predictions from M06-2X/6-311G*/PCM calculations suggest that the barrier for the 1,2-shift of the nitro group occurs with a barrier of 7.7 kcal/mol. With this prediction, is expected that the *ipso*-**2** will rearrange to the *ortho* intermediate under our reaction conditions. Together, the *ortho* and *ipso* trajectories afford 53% of the adduct, in comparison with 57% *ortho* product experimentally.

In general, the quantitative accuracy of the predicted selectivity for each of the ring positions supports the adequacy of the computational model and the accuracy of the proposed mechanism. These results strongly suggest that the electron transfer mechanism is not involved on the nitration of toluene, under these reaction conditions. This accurate prediction of the selectivity by a complete physical model should be compared with the failures of conventional qualitative explanations. There are many ways that people try to predict or explain the selectivity of the nitration of toluene. One standard way to explain the selectivity is based on the relative stability of the σ-complexes, but in this case this is a very poor prediction (Table 2 – 1). Another explanation is based on frontier molecular orbitals. These approaches can correctly predict that the *ortho* and *para* products should be favored, but they do not provide any quantitative idea of the amount of *meta* or *ipso* that should be obtained, or the ratio or *ortho* and *para* products. Other reactions, such as Friedel-Crafts acylation or bromination afford very different product ratios from that seen in nitration, even though the frontier-orbital considerations are the same in three reactions. Galabov, in an effort to explain the selectivity from a more quantitative approach, described a correlation of

observed selectivities with the calculated relative stability of σ-complexes.[66] However, for the nitration of toluene, this approach fails greatly for the *ortho* or *ipso* products. For the calculations done by Galabov, using B3LYP/6-311+G(2d,2p), it was found that the *ortho*-**2** is 4.0 kcal/mol less stable than *para*-**2**, and *ipso*-**2** is 3.1 kcal/mol less stable than *meta*-**2**, but the less stable σ-complex is formed to a greater extent in each case. It is no surprise that qualitative models and correlations fail, these models are incomplete physically. Here, we present a complete physical model that provides the first accurate quantitative prediction for the selectivity of the nitration of toluene.

The nature of selectivity. From trajectories using the simplified computational model, we can get some insight into the nature of the selectivity. This is because they show some key features. We explored three of these simplified models: 1) trajectories in which the explicit CH_2Cl_2 is switched out for a PCM implicit solvent model; 2) trajectories in explicit CH_2Cl_2 but lacking the BF_4^- counterion; and 3) trajectories lacking the counterion in implicit solvent. As explain before for the complete model in explicit solvent, trajectories with the NO_2^+ nitrogen loosely constrained at a distance from the aromatic carbons were equilibrated then extracted and integrated forward and backward in time with no constraint unit a σ-complex was formed.

From this process we found that in each of the models the *ortho-para* selectivity was crippled. In addition, these simplified models (1, 2 and 3), increased the *meta* product to 16%, 18% and 23%, and the *ipso* product rised to 12%, 4%, and 25%, respectively. These low selectivities are the product of trajectories that afford the σ-complexes a lot faster that the full model, with median times of 1150 fs, 800 fs, and

1025 fs, respectively. As can be seen from the two example trajectories in Figure 2 – 6, in each of the simplified models, the product is decided at an earlier stage (median C-N distancees of 2.9-3.2 Å) than for the complete model, and it is rare for the NO_2^+ to approach arene carbons without reacting.

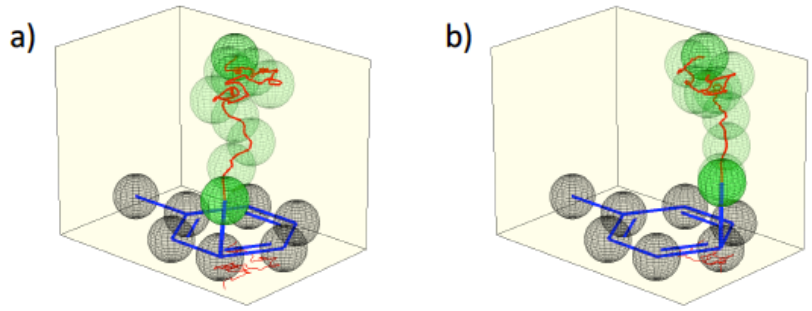


Figure 2 - 6: Motion of the nitrogen atom in typical trajectories using simplified models, relative to the average position of the toluene carbons. a) $NO_2^+BF_4^-$ in a PCM implicit solvent model. b) NO_2^+ (no counterion) in explicit CH_2Cl_2.

In general, these observations suggest that solvent dynamics are of key importance for the selectivity of the nitration of toluene. The attack of the NO_2^+ must be an entalpically downhill process. It is not initially, because the solvent and the counterion are arrange in a way that stabilizes better the positive charge of the NO_2^+. When selected trajectory points are subjected to steepest-descent optimization with the solvent and counterion frozen, C-N bond formation does not occur unless the initial C-N distance is less than ~2.0 Å. This observation is very different from what was seen with an implicit solvent model, where the process can be either barrierless, or involve

transition states with a C-N distance >2.5 Å (Figure 2 – 3c). At any distance smaller than 2.0 Å of the nitronium to the arene, the explicit solvent can be viewed as if it was acting like a force field on the reactants that prevents the formation of the σ-complex.

Even though the polarization of a solvent can adjust quickly to a redistribution of charge, full solvation requires reorientation of the molecular dipoles of the solvent. The process to achieve this takes time. In this case, the longitudinal and Debye dipolar relaxation times for CH_2Cl_2 are 900 fs and 2170 fs, respectively,[83-84] which is similar to the length of the trajectories. In the implicit solvent model the charge redistribution is too facile, because the solvation is assumed to be at equilibrium at all times, making the computationally unhindered trajectories unselective. In addition, the BF_4^- counterion must reposition to minimize charge separation versus the σ-complex. In the trajectories, the distance of the boron atom to the closest arene carbon shrinks from 5.4 Å at the beginning to 3.7 Å at the end of the trajectory. The counterion repositioning also takes time, and trajectories without this impediment are very unselective.

Our model shows that the NO_2^+ awaits an enthalpically downhill path to choose on of the regioisomeric σ-complexes. This is what gives the normal *ortho-para* selectivity. The energy surface for the reaction of the NO_2^+ with toluene can be viewed as the superposition of the energy effects of the solvent dipoles and counterion placement on the intrinsic energetics for NO_2^+ attack. Since the latter is energetically steeper when the attack is *ortho* or *para*, a downhill path is found faster for the formation of *ortho* and *para* complexes than for *meta* or *ipso*. This way, the selectivity reflects the different intrinsic energies of the pathways without involving transition states.

These results take us to two very important questions: *are there ever transition states after encounter? Do the transition states ever control the selectivity?* In HNO_3 / H_2SO_4 / water mixtures, the reaction of nitronium ions with toluene is not fully encounter-controlled. This is clear from the kinetic work done by Schofield and coworkers.[85] Their key observation was that the bimolecular rate constant for nitration reached a maximum in this medium when the benzene ring is activated by two alkyl groups, with further activation providing no further acceleration. Schofield concluded that the reaction of highly activated aromatics with NO_2^+ is encounter-controlled based on this leveling of the reactivity. Toluene, however, reacts at approximately 50% of the maximum rate, indicating that only 50% of the NO_2^+ / toluene encounters formed product. This can only be possible if there is a small but real dynamical bottleneck after encounter. These results suggested that, in this medium, there must be a TS or TSs after an intermediate.

As expected, benzene is less reactive than toluene; it reacts about 40 times slower than the encounter-controlled rate. Assuming a diffusion rate in H_2SO_4 / water of ~10^9 $M^{-1}s^{-1}$, the barrier for reaction of the intermediate would have a lower bound of about 7 kcal/mol (more if diffusional separation is slowed by an energetic barrier). The indisputable involvement of some form of intermediate would be consistent with the complexes calculated by Koleva *et al.*[68], though the barrier for its forward reaction would have to be somewhat higher than that calculated.

This characteristic of reactions in HNO_3 / H_2SO_4 / water mixtures is different from the reactions of NO_2^+ salts in less-coordinating organic solvents, in which all

observations are consistent with a process involving fully encounter-controlled rates. Reactions involving an encounter-controlled process could involve TSs after the encounter, but their kinetics do not require them. Contrary to the general assumption in literature, we have shown that the observation of positional selectivity after encounter in no way requires TSs. It is important to point out that the calculations presented here refer only to the absence of TSs in the reaction of toluene with $NO_2^+BF_4^-$ in CH_2Cl_2. It can be expected that TSs will more likely be present as the solvent used becomes more coordinating with the NO_2^+.

Even for the reaction conditions under study, TSs after encounter might be present if the reaction coordinate is defined differently. In this case, the barrierless slope shown in Figure 2 – 4 is based on a reaction coordinate defined by only the nitrogen arene – carbon distance. This coordinate is expected to be dominant in the energy of the system. However, TST is if anything, flexible, and in principle it may be possible to define TSs for the formation of the σ-complexes by using solvent coordinates and non-equilibrium solvation / solvent friction.[86] It is important to recognize that TSs are a useful chemical model, but they are not a scientific requirement. In this case, we could try to make this reaction fit into this model; however there is no point in doing so, because it cannot be used to make a realistic prediction of the selectivity. In contrast, the trajectories presented here provide both a quantitative prediction and a qualitative understanding of the nitration of toluene.

This approach solves a very important issue when TSs are used to explain selectivity. This is, TSs do not consider the possibility of a bifurcation or multifurcation

of pathways, which makes any TSs very unlikely to account for the selectivity. None of the studies presented here support the involvement of transition states in the selectivity of the reaction. However, our model accounts for the selectivity of the nitration of toluene without using transition states. Even when well-defined TSs can be located, as with the **4**‡, **5**‡, **6**‡, and **7**‡ series of TSs, 45 out of 53 sets of trajectories started from the various TSs afford mixtures of products. This shows that the normal description of selectivity as predicted from TS energies is unphysical even when defines TSs are located. It is not possible to exclude the possibility that there are some reaction conditions for which TSs can determine the selectivity, but since there is no evidence of this (specially or the reaction conditions under study here) this idea should stop been considered for nitration.

Conclusions

The assumption that a thin mechanism, one that considers only the TSs and the intermediates, was enough to understand the experimental observations for nitration of toluene forced a description of the mechanism. For this reaction, since it was found that the intermolecular and intramolecular selectivities were not explained by the same TS, it was proposed that *there had to be an intermediate* followed by a series of separate TSs to afford the different products. The nature of this intermediate was contested, and none of the proposals explained all observations. However, the view that there had to be an intermediate followed by product-determining TSs was unquestioned.

There is a big problem with this view, it fails drastically. An extensive effort to explain the regioselectivity of the nitration of toluene using TS energies in implicit solvent failed to provide reasonable predictions. Calculations did not even support the idea that the selectivity can be related to TS energies, this is because most TSs lead to two products. Mechanistic details are important to the degree that they allow the prediction of experimental observations. From this point, even if TSs are present in some nitrations, they may simply be unimportant.

In contrast, the regioselectivity for the nitration of toluene with $NO_2^+BF_4^-$ in CH_2Cl_2 can be accurately predicted with a mechanism that does not involve an intermediate prior to the σ-complex and not TSs after the encounter. The prediction is based on a complete physical model, includes explicit solvent and the counterion, allowing fully for their dynamics, and provides the first quantitatively accurate prediction of the selectivity. The success of the quantitative predictions obtained from this model supports the accuracy of the proposed mechanism.

The general idea has always been that when a reaction passes through a simple single TS, the solvation at the TS will be approximately at equilibrium. This idea allows the consideration of solvent effects on TS energies in a way that simulates the ordinary equilibrium-solvation effects on ground-state energies, this has the effect of keeping the solvent dynamics to a minimum. However, this simplification does not apply when the reaction coordinate is more complicated and it does not apply when there is no TS. This is the case in the nitration of toluene. Our results showed that solvent dynamics play a very important role in the nitration of toluene. We found that even though it faces an

uniformly exergonic slope (downhill in free energy at equilibrium), the approach of the nitronium ion to the toluene is slowed down by solvation and counterion positioning that is not at equilibrium. The process for reorganization of the solvent and the counterion takes time, and the resulting slow, and often reversing approach allows the nitration to be selective. Without TSs, the decision of which product is going to be formed is made late in the approach when the energetic attraction of the reactants finally overcomes the energetics related to the reorganization of the solvent and counterion. These ideas are clearly qualitative at this point, and greater understanding of the nature of the selectivity on reactions involving downhill slopes, particularly in polar solutions, will need to be develop. Our results suggest novel methods for the control of selectivity in these reactions.

Experimental and Computational Procedures

Nitration of toluene using nitronium tetrafluoroborate in CH_2Cl_2. Example procedure. To a rapidly stirred mixture of 0.72 g (5.4 mmol) of nitronium tetrafluoroborate in 217 mL of CH_2Cl_2 was added, in one portion, a mixture of 4.6 mL (3.99 g, 43.3 mmol) of toluene and 217 mL of CH_2Cl_2. The reaction mixture was stirred for 2 h at 25 ºC, and the reaction was quenched by addition of 50 mL of water. The aqueous phase was extracted with three 50-mL portions of CH_2Cl_2. The combined organic layers were rinsed with 50 mL of brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was then analyzed directly by ^1H NMR. The characteristic peaks for the products were: *o*-nitrotoluene: ^1H NMR ($CDCl_3$):

δ 2.58 (s, 3H), 7.32 (m, 2H), 7.48 (t, J=8 Hz, 1H), 7.94 (d, J=8 Hz, 1H); *m*-nitrotoluene: ^{1}H NMR ($CDCl_3$): δ 2.42 (s, 3H), 7.38 (t, J=7.8 Hz, 1H), 7.47 (d, J=7.8 Hz, 1H), 7.95 (s, 1H), 7.97 (s, 1H); *p*-nitrotoluene: ^{1}H NMR ($CDCl_3$): δ 2.44 (s, 3H), 7.29 (d, J=8.2 Hz, 2H), 8.08 (d, J=8.2 Hz, 2H).

Approximately 0.6% of material tentatively identified as 2,4-dinitrotoluene was observed under these conditions. This assignment was made based on characteristic peaks at δ 8.78 (d, J=2.3 Hz), 8.31 (d of d, J=8.5 and 2.3 Hz), and 7.54 (d, 8.5 Hz).

Nitration of toluene using nitronium tetrafluoroborate without solvent. To 10.0 mL (8.67 g, 94.4 mmol) of toluene was added, in one portion, 0.63 g (4.7 mmol) of nitronium tetrafluoroborate. The resulting mixture was stirred for 1 h at 25 °C. The reaction was quenched by addition of 15 mL of water. The organics were washed with 15 mL of brine and dried over anhydrous Na_2SO_4, then analyzed directly by ^{1}H NMR.

Product ratio determination. The product ratios were determined from the crude mixture by ^{1}H NMR. The signals used for the product ratio determination were those for the aromatic protons *ortho* to the nitro group in each compound, allowing for the number of hydrogens in the signals integrated. The percentage of each isomer, the average, standard deviation and 95% confidence interval are shown in Table 2 – 2.

Table 2 - 2: Product ratios, averages, standard deviations and 95% confidence intervals for the nitration of toluene.

	Para (%)	**Ortho (%)**	**Meta (%)**
	41.05	57.03	1.93
	41.94	56.02	2.04
	41.25	56.93	1.82
	40.64	57.08	2.28
	40.84	57.10	2.06
	40.73	57.13	2.14
Average	41.07	56.88	2.05
Stdve.	0.48	0.43	0.16
95% conf.	0.50	0.45	0.17

Product ratio vs concentration for nitration of toluene. To evaluate the possible role of more complicated mechanistic possibilities on the nitration regiochemistry, the selectivity was examined at a range of concentrations, including neat toluene, 2 M, 1 M, 0.1 M, and 0.01 M, by procedures matching or analogous to those described above. The results are shown in Table 2 – 3.

Table 2 - 3: Product ratios vs concentrations for nitration of toluene.

Concentration	**Para (%)**	**Ortho (%)**	**Meta (%)**
No solvent	41.1	56.3	2.6
2 M	40.7	56.6	2.7
1 M	39.5	57.9	2.7
0.1 M	41.1	56.9	2.0
0.01 M	41.1	56.6	2.2

General computational procedure. Calculations of structures, energies, and frequencies employed default procedures in Gaussian09 unless otherwise noted. Complete structures and energetics are provided in sections below. All absolute energies are in Hartrees. All relative energies are presented in kcal/mol.

The program suite PROGDYN used for dynamics is a series of component programs written as either Unix shell scripts or awk programs. Gaussian09 was used to calculate the forces at each point in trajectories. A full description of PROGDYN including listings of the subprograms can be found in the appendix. The latest version of this program can be obtained from Daniel Singleton of Texas A&M.

The program PROGMC is a new program consisting of a series of component programs written as either Unix shell scripts or awk programs. Gaussian09 was used to calculate the raw energies for each test geometry, and PROGMC adjusts these energies by biasing potentials and a potential used to maintain a spherical solvent cluster. A full description of PROGMC including listings of the subprograms can be found in the appendix.

IRCs were not conducted for all structures; rather, they were only conducted for structures where an examination of the transition vector left the outcome of the IRC in reasonable doubt. In some cases, particularly when IRC calculations failed, trajectory calculations were carried out to determine the products from a transition structure, and it was presumed that the IRC would lead to the major product from the trajectories. There are cases where this assumption would be incorrect, but in those cases we would argue that trajectories provide a *better* measure of the product from a transition structure than

an IRC.

Initialization of trajectories and additional details on trajectories. Trajectories were initialized in differing ways depending on the details of the calculation. All trajectories started from transition structures (simple potential energy saddle points) or canonical variational transition structures (CVTSs) were quasiclassical. This includes trajectories started from **4a**‡, **4b**‡, **4c**‡, **5a**‡, **5b**‡, **5c**‡, **6a**‡, **6b**‡, **6c**‡, and related transition structures. For quasiclassical trajectories, each normal mode in the transition structure of interest was given its zero-point energy plus a Boltzmann distribution of quantized vibrational energies. The desired energy in each of the normal modes of the transition structure was mapped from a random number generator to a Boltzmann distribution set at 25 °C. The phase of each of the normal modes was mapped from a Gaussian distribution of random numbers. This distribution is not correct for a classical oscillator but would be approximately correct for a quantum oscillator in its ground state (only ignoring mode displacements outside of the classical limit), and has the advantage that a larger portion of the trajectories start with an energy approximating the initially desired energy. The sign on the velocity of the normal modes was randomized. After an energy/force calculation on the initial geometry, the total initial energy was calculated and the trajectory was thrown out if the energy did not agree satisfactorily (within 1 kcal/mol) with the desired energy. (This is a variation of the conventional practice of scaling energies.) The mode corresponding to the transition vector was treated classically. A sample PROGDYN parameter file (progdyn.conf) is given in a later section.

The trajectories in explicit solvent and related supporting studies were fully classical, and their initation is described in subsequent sections.

PMF trajectories initialization, PMF in a solvent cube, and extended data. The process for generating starting structures for trajectories in a sphere of 101 CH_2Cl_2 molecules was circuitous. Initial structures were generated by surrounding molecules of toluene and NO_2^+ with 102 CH_2Cl_2 molecules, using a cube of CH_2Cl_2 geometries generated with an Excel spreadsheet. The distance between the aromatic ring carbons and the ipso and para carbons of toluene was constrained at ≈4 Å using the *fixedatom* resource in PROGDYN, and six random trajectories were initiated at 1000 Kelvin using a PM3 surface. The solvent molecules were forced into a cube with 22.4 Å sides using the *boxon* facility in PROGDYN, and the six trajectories were equilibrated at 1000 Kelvin for 5 ps, then cooled slowly to 25 °C using the thermostat facility in PROGDYN with thermostatmult set at 0.999 (removing 0.1% of the energy per fs), and equilibration at 298 K was continued for 5 ps.

The set of six trajectories was then duplicated to give two sets. The first set of six trajectories will be used in a later section. For the second set of six, a CH_2Cl_2 molecule was converted into a BF_4^- molecule. The latter were equilibrated for 5 additional ps in PM3 calculations, using at this stage a harmonic potential to maintain a 3 Å separation between the NO_2^+ and the BF_4^- ions. The two sets of six trajectories were then equilibrated at 25 °C with only the nitrogen atom – arene carbon constraint for 5 ps in ONIOM calculations using M06-2X/6-311G* for the toluene / NO_2^+ and PM3 for the BF_4^- (when present) and CH_2Cl_2.

The six sets of trajectories including $NO_2^+BF_4^-$ were then duplicated five times (for a total of 36 sets of trajectories) and dispersed using a series of interlocking-sphere biasing potentials (see the section below for details) using the *applyforce* facility in PROGDYN. All other constraints were turned off. The biasing potential sphere radii and number of assigned trajectories for these potentials were 2.1 Å (5), 2.2 Å (3), 2.5 Å (3), 2.8 Å (3), 3.1 Å (3), 3.4 Å (3), 3.7 Å (3), 4.0 Å (3), 4.3 Å (2), 4.6 Å (2), 4.9 Å (2), 5.2 Å (2), and 5.5 Å (2). These trajectories were equilibrated for 5 ps, then nitrogen-carbon distance data was collected and analyzed using the weighted-histogram analysis method (see reference in main text and sample files in the appendix).

A total of 240 ps of MD was obtained, and the results are shown in Figure 2 – 7. The PMF exhibits the same absence of a barrier seen later. It was judged however that the use of a cubic box of solvent was non-optimum, in part because the rigid box facility in PROGDYN is relatively subject to edge effects and in part because of the non-isotopic distribution of solvent molecules.

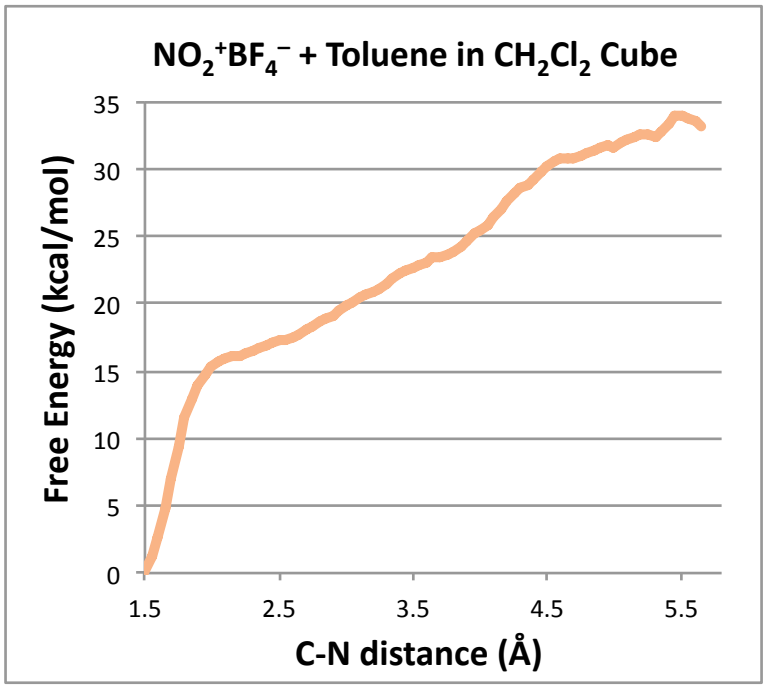


Figure 2 - 7: Potential of mean force curve for approach of $NO_2^+BF_4^-$ to toluene in a 22.4 Å cube of 101 CH_2Cl_2 molecules

Each of the cubic structures was then molded into a sphere with a soft 25.8 Å diameter using the *sphereon* facility in PROGDYN, and equilibrated for 5 ps after achieve a spherical shape. Once in a sphere, the N atom of the NO_2^+ was constrained to the center of the sphere by a weak harmonic potential (with k = 0.119 kcal/mol/Å^2) to the middle of the sphere, using the *zeroatom* facility in PROGDYN. The sphere was maintained with a density of 1.3 by a harmonic restoring potential (with k = 11.86 kcal/mol/Å^2) on atoms outside of 12.9 Å from the center of the sphere. That is, a force is applied to atoms that are outside of 12.9 Å from the center of the sphere, along a vector toward the center of the sphere. The magnitude of the force was set to (distance to

center -12.9 Å) x 11.86 kcal/mol/Å^2. These parameters are set with the "*sphereon* 1", "*spheresize* 12.9", and "*sphereforce* 0.01" keywords in PROGDYN. The appendix shows the complete PROGDYN parameter file (progdyn.conf) for these trajectories.

Duplication of trajectories and dispersal with differing biasing potentials ultimately generated a total of 66 separate trajectories from which MD data was collected. In all cases care was taken to maximize the independence of separate trajectories. In some cased the trajectories were cut short and were not restartable. This arose from a bug in PROGDYN; if a PROGDYN run cannot write to disk (as occurs when a disk quota maximum is reached), the files necessary for restarting runs can be lost. As a result, the length of the separate trajectories varies from 4 ps to 52 ps. The biasing potential sphere radii and number of assigned trajectories for these potentials were 1.9 Å (7), 2.0 Å (7), 2.1 Å (6), 2.2 Å (11), 2.35 Å (6), 2.5 Å (3), 2.8 Å (4), 3.1 Å (3), 3.4 Å (4), 3.7 Å (3), 4.0 Å (3), 4.3 Å (2), 4.6 Å (2), 4.9 Å (2), 5.2 Å (2), and 5.5 Å (2).

Product-forming trajectories for the full model. To generate product-forming trajectories, PMF trajectories above in which the interlocking-sphere biasing potential was zero at 3.4-4.0 Å were used as "feeder" trajectories to provide starting points. At 250 fs intervals the helper program *prodynsam* (listed in the apendix) was used to create a *geoPlusVel* file for use in PROGDYN. The *progdynsam* program leads to trajectories with all atoms moving at their current velocity. Each resulting unconstrained trajectory was integrated forward and backward in time until one of the regioisomers of **2** (defined by a C-N distance of <1.6 Å) was formed. A typical starting point for product-forming

trajectories is shown below. The solvent molecules are seen clearly but the reactants are somewhat obscured (Figure 2 – 8).

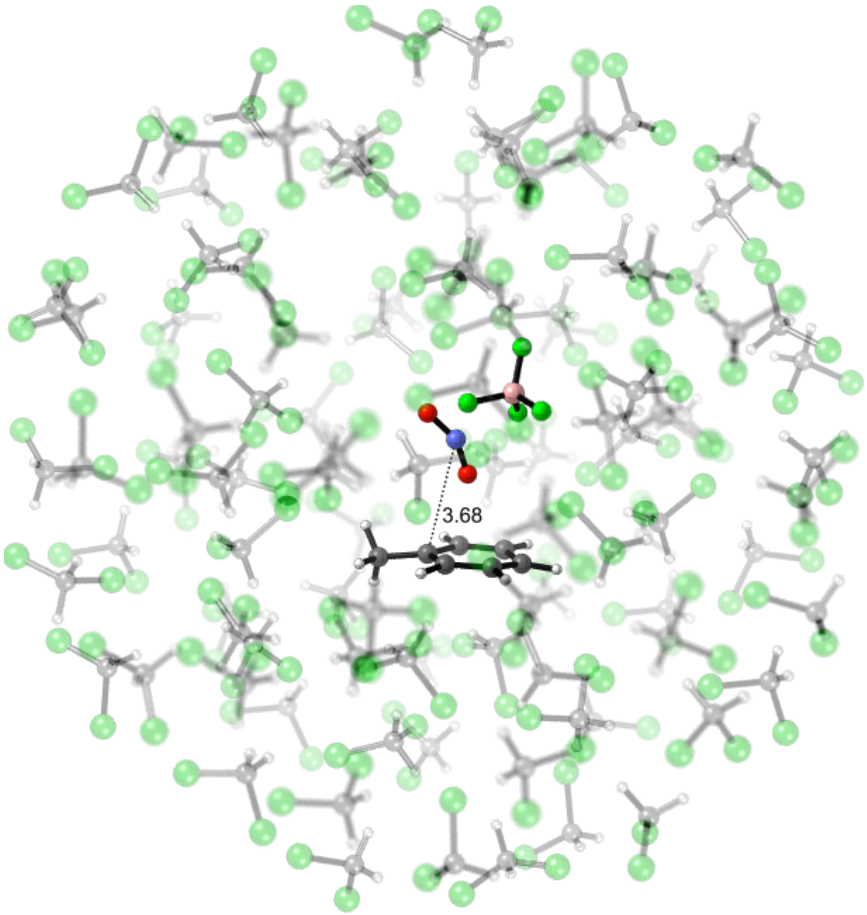


Figure 2 - 8: Typical starting point for product-forming trajectories

Product-forming trajectories using $NO_2^+BF_4^-$ in implicit solvent. A series of six trajectories containing only toluene and $NO_2^+BF_4^-$ were created by taking six of the PMF trajectories in implicit solvent from above and deleting all of the solvent molecules, then

continuing the trajectories with a PCM implicit solvent model for CH_2Cl_2 and the same interlocking-sphere biasing potential as in the source trajectories. The biasing potential sphere radii and number of assigned sequences for these potentials were 3.4 Å (1), 3.7 Å (2), 4.0 Å (2), and 4.3 Å (1). These "feeder" trajectories were then equilibrated and thermostated at 25 °C for 2 ps. The energy surface was ONIOM / PCM(CH_2Cl_2), using M06-2X/6-311G* for the toluene and NO_2^+ and PM3 for the BF_4^-.

After equilibration, at 250 fs intervals the helper program *prodynsam* (listed in the apendix) was used to create a *geoPlusVel* file for use in PROGDYN. The *progdynsam* program leads to trajectories with all atoms moving at their current velocity. Each resulting unconstrained trajectory was integrated forward and backward in time until one of the regioisomers of **2** (defined by a C-N distance of <1.6 Å) was formed, or the NO_2^+ dissociated as judged by a C-N distance > 5.0 Å.

A total of 151 results were obtained:

32 – dissociated

48 – formed the para product

19 – formed the meta product

38 – formed the ortho product

14 – formed the ipso product

Product-forming trajectories using NO_2^+ in implicit solvent. A series of six trajectories containing only toluene and NO_2^+ were created by taking six of the PMF trajectories in implicit solvent from above and deleting all of the solvent molecules and

the BF_4^-, then continuing the trajectories with a PCM implicit solvent model for CH_2Cl_2 and interlocking-sphere biasing potentials with radii 3.7 Å. These "feeder" trajectories were then equilibrated and thermostated at 25 °C for 2 ps. The energy surface was M06-2X/6-311G*/PCM(CH_2Cl_2).

After equilibration, at 250 fs intervals the helper program *prodynsam* (listed in the apendix) was used to create a *geoPlusVel* file for use in PROGDYN. The *progdynsam* program leads to trajectories with all atoms moving at their current velocity. Each resulting unconstrained trajectory was integrated forward and backward in time until one of the regioisomers of **2** (defined by a C-N distance of <1.6 Å) was formed, or the NO_2^+ dissociated as judged by a C-N distance > 5.0 Å.

A total of 149 results were obtained:

0 – dissociated

41 – formed the para product

34 – formed the meta product

37 – formed the ortho product

37 – formed the ipso product

Product-forming trajectories using NO_2^+ in explicit solvent. A previous section described the creation of a set of six trajectories including toluene and NO_2^+ but no counterion in 102 explicit CH_2Cl_2 molecules. After the previously described equilibration, these trajectories were continued with constrained C-N distances of ≈4.0 on the ONIOM energy surface. At 250 fs intervals the helper program *prodynsam* (listed

in the apendix) was used to create a *geoPlusVel* file for use in PROGDYN. The *progdynsam* program leads to trajectories with all atoms moving at their current velocity. Each resulting unconstrained trajectory was integrated forward and backward in time until one of the regioisomers of **2** (defined by a C-N distance of <1.6 Å) was formed, or the NO_2^+ dissociated as judged by a C-N distance > 5.0 Å.

A total of 209 results were obtained:

0 – dissociated

67 – formed the para product

37 – formed the meta product

97 – formed the ortho product

8 – formed the ipso product

It should be noted that these trajectories were conducted in a cube of solvent, not a sphere. Exploratory studies did not find any significant difference between product-forming trajectories in a cube versus a sphere.

Monte Carlo starting points, equilibration, and extended data. The starting geometries for a series of 48 Monte Carlo geometry sequences were taken from MD structures in the later half of their data collection. The biasing potential sphere radii and number of assigned sequences for these potentials were 1.8 Å (6), 2.0 Å (6), 2.1 Å (5), 2.2 Å (6), 2.35 Å (6), 2.5 Å (2), 2.8 Å (2), 3.1 Å (3), 3.4 Å (2), 3.7 Å (2), 4.0 Å (2), 4.3 Å (2), 4.6 Å (2), and 4.9 Å (2). The resulting geometries were equilibrated for 1000 steps

when the biasing potential was unchanged versus the MD source of the geometry, and for 5000 steps when the biasing potential was changed versus the MD source.

As internal checks of the Monte Carlo data, we monitored whether the overall average C-N distance varied systematically as the sequences proceeded, and we monitored whether independent sequences provided equivalent data. Some of the data obtained failed these internal checks, and this data was not included in Figure 2 – 3 of the main text. This requires some explanation.

In a Monte Carlo program, a central problem is how to explore coordinate space in a fully representative way in as few of steps as possible while keeping a reasonable percentage of the steps acceptable. PROGMC approaches this problem by dividing the system into molecules, performing translations and rotations on the molecules as a whole, stepping the bond lengths in each molecule by necessarily relatively small steps, and stepping angles and dihedral angles by larger steps using an algorithm that steps along two vectors that are orthogonal to the bond stretch and each other. The program was judged nicely efficient at dealing with the NO_2^+, BF_4^-, and 101 CH_2Cl_2 molecules. It had trouble however dealing with the large distortions of the toluene ring that are associated with NO_2^+ attack. This trouble was associated with a common problem with ring structures and internal coordinates; small changes in internal coordinates in rings can have large effects on the "last" bond in a ring, that is, the one that is not directly determined by an internal coordinate. This is a well-known solvable problem but is not solved yet in the current code. The code instead decreased the motion of atoms in the toluene ring, but this slows large geometry changes in the ring. Because of the problem

with slow equilibration in the area of the surface associated with NO_2^+ attack, we did not include that portion of the data in Figure 2 – 4. Figure 2 – 9 displays the complete data. The Monte Carlo results still show the same qualitative pattern as the MD data, but, lacking a full exploration of the space associated with **2**, the energy dip in this area (with a C-N distance less than 1.85 Å) is far less pronounced.

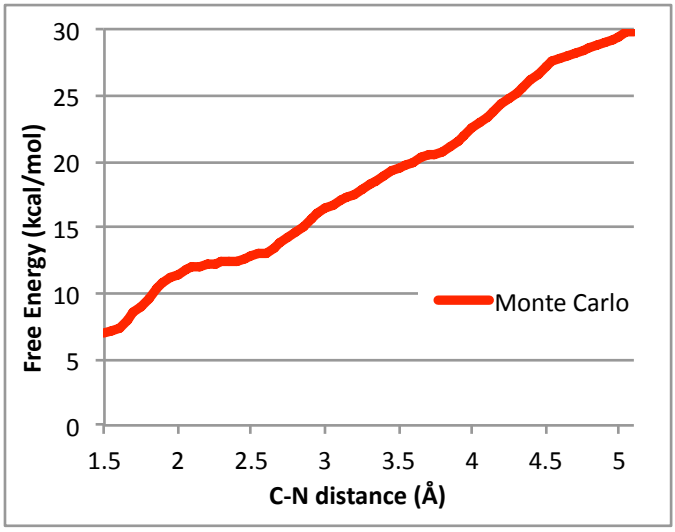


Figure 2 - 9: Extended version of the Monte Carlo data from Figure 2 – 3 of the main text showing all available data

The interlocking sphere biasing potential. The use of simple biasing potentials based on the distance of the nitrogen atom from a chosen carbon atom, such as the *para* carbon, fails. The failure occurs because the NO_2^+ remains free to attack the other aromatic carbons, and it invariably does so except when the biasing potential sets very

short C-N distances. This problem was avoided using the more complicated biasing potential to be described here. The next section discusses in more detail the meaning of the PMF curve for this complex biasing potential.

The MD and Monte Carlo calculations employed biasing potentials that were based on interlocking spheres centered on the arene ring carbons. The surface of the spheres represents the zero of the potential, and the applied potential was 0.5 * 118.6 kcal/mol/Å^2 * r^2 where r is the distance of the nitrogen atom from the closest surface point of the spheres. For Monte Carlo calculations, this potential was simply added to the energy of the system. For MD calculations, the nitrogen atom and the carbon atom at the center of the closest sphere were subjected to a restoring force along their internuclear axis.

The first picture below illustrates the interlocking spheres when at a radius of 2.5 Å from the carbon nuclei, using transparency to show the positions of the carbon nuclei (Figure 2 – 10). It should be noted that the spheres move with the motion of the carbon atoms, and that no sphere was place around the methyl-group carbon. The second picture shows the solid zero-potential surface (Figure 2 – 11).

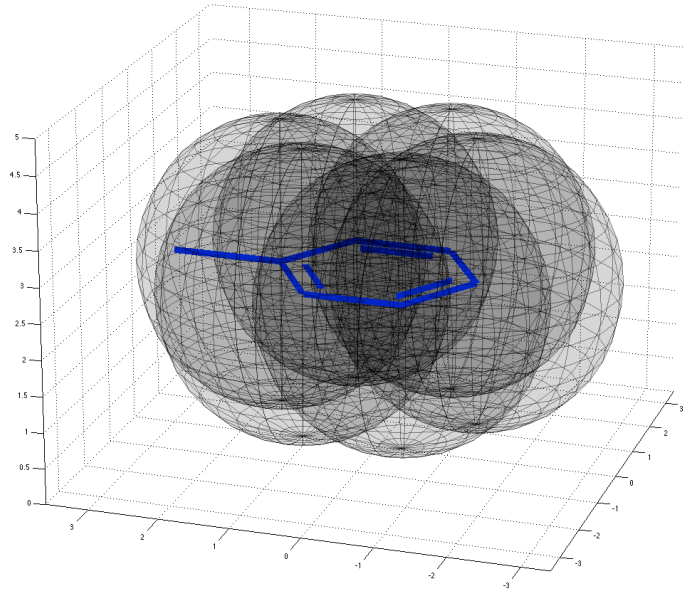


Figure 2 - 10: Interlocking spheres when at a radius of 2.5 Å from the carbon nuclei, using transparency to show the positions of the carbon nuclei

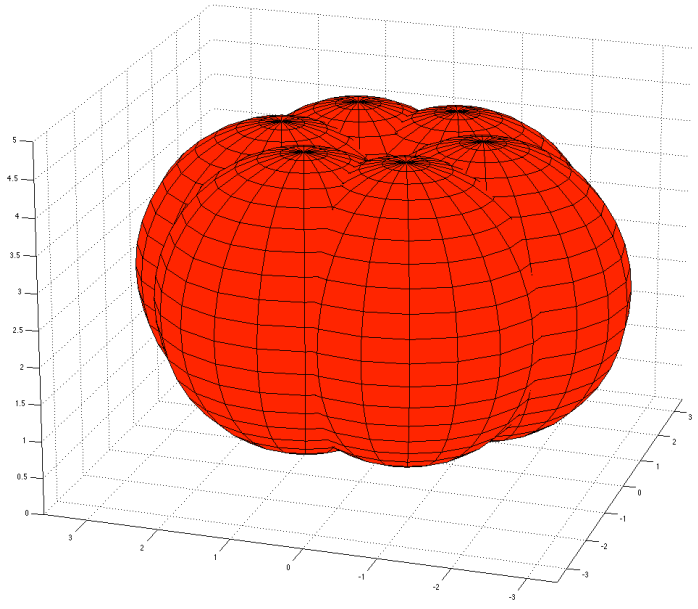


Figure 2 - 11: Solid zero-potential surface

Additional discussion of the meaning of the Figure 2 – 3 PMF Curves. The interlocking-sphere biasing potential that was employed lets the NO_2^+ roam from carbon to carbon in the MD and Monte Carlo simulations. However, the energetics of the system can restrict the roaming, depending on the distance of the NO_2^+ from the ring. Some discussion of these effects on roaming and how they affect the meaning of the PMF curves will be given here.

Table 2 – 4 below shows the radius of the spheres in the biasing potential (which we will simplistically call the "C-N distance"), the total MD time for each radius, the number of "switches" for each radius where a "switch" is a change of closest carbon from one carbon to another (a simple measure of the roaming of the NO_2^+), the average time between switches, and the percentage of the time that the MD trajectories were nearest the *para*, *meta*, *ortho*, or *ipso* carbons.

We first consider the roaming of the NO_2^+ at relatively long C-N distances. In a medium range between C-N distances of 2.8 Å and 4.3 Å, switches are common. At the longest C-N distances (4.6 Å or greater), switches become less common. This is likely to be simply a geometry effect – the spheres have become bigger and their surface near the plane of the aromatic becomes accessible, so the NO_2^+ must roam a greater average distance to switch from carbon to carbon. At C-N distances between 3.4 and 4.0 Å, the distribution of *para* / *meta* / *ortho* / *ipso* carbons as closest to the NO_2^+ appears roughly statistical (allowing for a factor of 2 as appropriate), as mentioned in the main text. The distribution also appears to be statistical at longer distances, though there is more fluctuation in the numbers, perhaps due to the lower total time of the MD simulations.

Table 2 - 4: Roaming Information in MD trajectories with a biasing potential

Potential sphere radius	Total time (fs)	"Switches"	Time (fs) / switch	*% para*	*%meta*	*%ortho*	*%ipso*
2 Å	125539	18	6974	45	15	35	5
2.1 Å	129184	39	3312	91	2	7	0
2.2 Å	140594	271	519	57	9	18	16
2.35 Å	108354	682	159	35	9	27	29
2.5 Å	107698	1025	105	26	10	20	44
2.8 Å	119991	2102	57	4	7	32	57
3.1 Å	47370	767	62	37	35	23	5
3.4 Å	47016	1286	37	17	25	35	23
3.7 Å	46588	1296	36	20	25	35	20
4 Å	46943	1989	24	24	32	30	14
4.3 Å	28072	1029	27	20	29	33	18
4.6 Å	26652	546	49	18	29	20	32
4.9 Å	20823	316	66	15	33	32	20
5.2 Å	19389	165	118	11	43	31	16
5.5 Å	15219	79	193	17	36	39	8

At C-N distances of 2.8 and 2.5 Å, the NO_2^+ appears to prefer to be near the ipso carbon. In this distance range we see a similar preference for the NO_2^+ to be near the *ipso* carbon in PCM calculations. As mentioned in the before, the most stable transition structure for attack of NO_2^+ on toluene in PCM calculations was one for attack at the *ipso* carbon. At 2.35 and 2.2 Å, a preference for the NO_2^+ to be near the *para* carbon emerges.

At distances shorter than 2.2 Å, there is a significant complication in the data. That is, switches are sufficiently uncommon that we can no longer expect the ratio of the closest carbons to reflect a thermodynamic preference. Random statistical effects impact all of the *para* / *meta* / *ortho* / *ipso* ratios in the table, but at the shortest distances the

ratios depend on the starting points. The 2 Å data contains a significant amount of time in which the *meta* and *ipso* carbons were closest simply because the starting points afforded significant amounts of these points. The 2 Å data should be recognized as a range that includes C-N distances down to 1.5 Å. At the shortest distances it is far more stable for the NO_2^+ to be near the *para* carbon. When trajectories switch from *meta* or *ipso* to *ortho* or *para* and stay there for > 500 fs, they never switch back. For this reason, the *meta* and *ipso* 2 Å data are questionable, since they do not appear to be the result of a full equilibration. A reanalysis leaving out this data had no significant effect on the MD PMF curve.

This brings up an important caveat on our conclusions. That is, because we have no fully-defensible data for MD with the NO_2^+ nearest the *meta* or *ipso* carbons, we do not know whether there is a barrier for the formation of the *meta* or *ipso* isomers of **2**. We can only say that there is no free-energy barrier along the C-N distance coordinate for attack at the *para* and *ortho* carbons.

CHAPTER III

DYNAMICS AND THE NATURE OF THE SELECTIVITY IN THE FRIEDEL-CRAFTS ACYLATION OF HIGHLY REACTIVE AROMATICS

Introduction

For many years the understanding of the reactivity and regioselectivity of electrophilic aromatic substitution reactions, and their mechanistic understanding was very important. Most of the observations associated with this type of reactions are usually understood within a limiting mechanistic framework (Figure 3 – 1) involving electrophilic attack via TS **1** to afford an intermediate cation **2**, generally referred to as a σ-complex.[87-89] Later, this intermediate loses a proton to form the final product **3**. There are multiple observations that support this simple mechanistic pathway, but a cornerstone observation is a general correspondence between the stability of the σ-complex intermediate, the reactivity of the aromatic, and the regioselectivity of product formation. The relationship between the reactivity of the aromatic and the selectivity of these reactions was described quantitatively in the "Brown selectivity relationship".[90] Brown, in a series of studies in the 1950s, found that the reactivity and the isomer selectivity correspond in many simple electrophilic aromatic substitution reactions.[91-99] This observation is evidence that suggest that a single TS has to be both rate limiting, and product determining, which is expected for a TS that resembles **1** leading to the σ-complex.

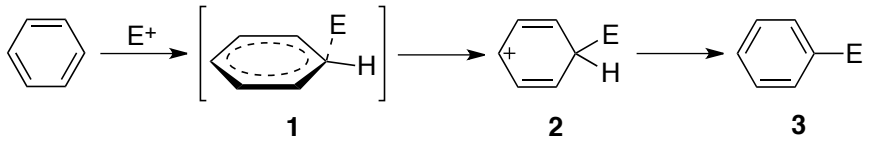


Figure 3 - 1: General mechanistic scheme for electrophilic aromatic substitution

An important assumption for this mechanistic proposal is that any particular TS can only lead directly to a single product. However, in some cases, the reactants pass the rate limiting TS and proceed to form two or more products without a barrier.[100-103] This kind of behavior is what we refer to as a *bifurcating energy surface.* The implications of this kind of dynamic effect toward experimental observations has only recently begun to be appreciated.[14, 19, 26, 71-73, 104-107] In this chapter we present evidence that supports the involvement of a bifurcating energy surface in an electrophilic aromatic substitution of highly reactive aromatics. This observation leads to a broader understanding of selectivity in reactions of highly reactive substrates and electrophiles.

When considering whether a bifurcating energy surface might be involved in an electrophilic aromatic substitution, we reasoned that it was best to explore reactions in which the reaction's electrophilic addition involves an "early" TS. This is because, when the TS for the addition of an electrophile to an arene is "late", the electrophile will have decided to form a bond with a particular carbon and no dynamic choice of products is possible. This is usually the case with most electrophilic aromatic substitutions. However, an early TS could provide the possibility that the regioselectivity of the electrophilic attack might not be decided yet. Using Hammond's postulate,[108] we can

expect that an early TS will be favored when highly reactive electrophiles are reacted with activated arenes.

Interestingly, the mechanism of this kind of aromatic substitution has been the most controversial. When studying electrophilic aromatic substitutions, Olah found a series of reactions of strong electrophiles that display low intermolecular substrate selectivity but high positional selectivity.[47] As described in the previous chapter, these observations lead Olah to propose that the inter- and intramolecular selectivities were determined in a rate-limiting formation of a π-complex **4** followed by intramolecular selectivity determined in the formation of the σ-complex.

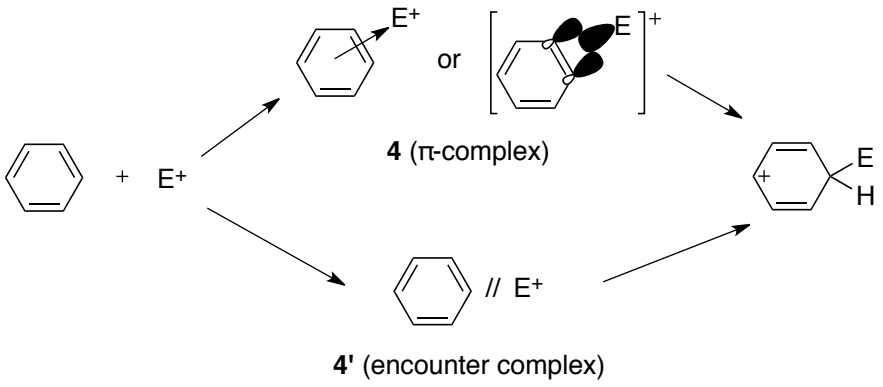


Figure 3 - 2: Proposed mechanistic pathways based on the inter- and intramolecular selectivities

This proposal was very criticized from two perspectives. The first one been related to the nature of the intermediate. In general, it was argued that the π-complex

intermediate was not real, and that it was possible that this step was macroscopic mixing or a diffusional encounter process.[48] Eventually, the π-complex intermediate and the encounter complex process were combined;[50] however, there were some inconsistencies that could not be explain. The general and accepted perspective was that some kind of irreversible intermediate had to be involved in order for the reaction to be selective.

The second perspective was related to how often the selectivity relationship failed. In a series of analyses of toluene / benzene rate ratios and selectivities, anomalies were found to be rare.[51-52] Some apparent failures of the Brown selectivity relationship have been proposed to be misguided.[109-110] Despite this criticism, some anomalies in the selectivity of these reactions cannot be rationalized, and this seems particularly the case with arenes more reactive than toluene in their reactions with strong electrophiles.[46, 50, 56, 64, 111-113]

The Brown relationship between intermolecular substrate selectivity and intramolecular positional selectivity in electrophilic aromatic substitution is analogous to a well-known phenomenon in KIEs. This is, when a reaction involves a single rate-limiting / product-determining steps, intramolecular and intermolecular KIEs must correspond in a consistent manner. If this is not true, then the rate-limiting and product-determining steps must be separate. In a conventional analysis, a lack of correspondance of inter- and intramolecular KIEs was considered to be evidence that an intermediate was involved in the reaction; however, as is particularly relevant here, we found that the dynamics of bifurcating energy surfaces can result in a reaction having two kinetically

distinguishable steps *without an intermediate.*[105] This idea will let us explain Olah's observations without the involvement of an intermediate.

In order to understand what dynamic effects are involved in electrophilic aromatic substitution, we applied a combination of intermolecular and intramolecular KIEs as an advantageous form of the Brown selectivity relationship. In the reaction of veratrole with a week electrophile, the relationship holds, supporting the conventional mechanism. However, this is not true for reactions involving a more reactive electrophile, giving unusual intramolecular KIEs that cannot be rationalized by a conventional mechanism. The combination of the experimental KIEs, standard theoretical calculations, and trajectory studies support a key role of dynamics in the selectivity of electrophilic aromatic substitutions, in this case the Friedel-Crafts acylation.

Results and Discussion

The Friedel-Crafts acylation of veratrole (**5**) was chosen for study.[114] We chose veratrole because it is very reactive toward electrophilic aromatic substitution reactions, and this high reactivity was, interestingly, used by Dewar as an argument for the importance of π-complexes. The C4 and C5 positions of veratrole are equivalent in the absence of isotopic substitution, and a high selectivity for substitution at this position is generally observed. Particularly, the acylation of veratrole presents a high selectivity, since no product was observed corresponding to the substitution at C3. However, the intermolecular substrate selectivity of acylation is in a medium range among

electrophilic aromatic substitution reactions.[115] For the purpose of this study, the acylation of veratrole was done using two different reaction conditions ($AlBr_3$ and $AgClO_4$) (Figure 3 – 3). Under both reaction conditions only one product was observed, corresponding to the C4 or C5 substitution (**6**).

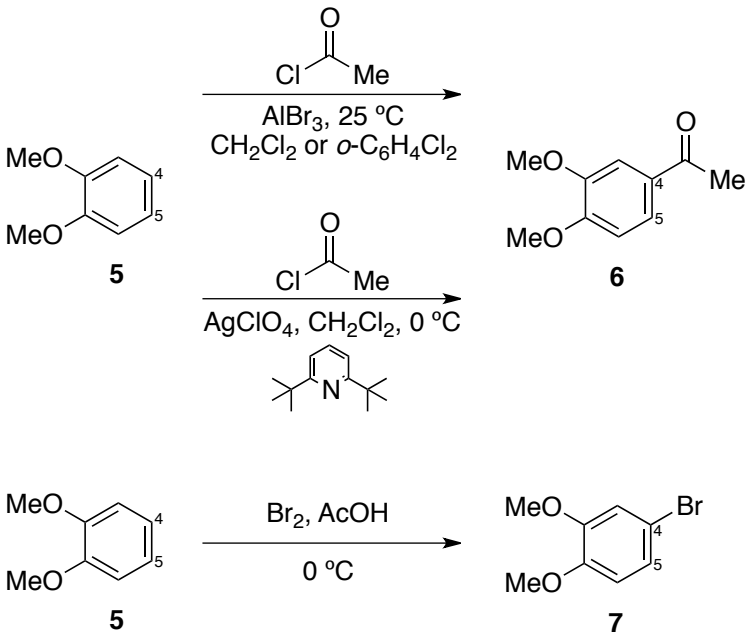


Figure 3 - 3: Friedel-Crafts acylation reactions under study, and the bromination reaction used for mechanistic comparison.

In order to compare the results of the acylation with a reaction expected to follow the conventional electrophilic aromatic substitution mechanism, we decided to study the bromination of veratrole in acetic acid at 0 ºC. Under these conditions, electrophilic attack appears to involve a late transition state for formation of a σ-complex, as the

reactivity of diverse arenes closely parallels the stability of corresponding σ-complexes.[47] As additional mechanistic evidence, it is well known that bromination in acetic acid follows the Brown selectivity relationship.[90] The bromination of veratrole affords 4-bromoveratrole (**7**) in nearly quantitative yield, affording approximately 0.4% of the isomeric 3-bromoveratrole.

To help with the interpretation of the kinetic isotope effects (KIEs) of the veratrole reactions, the Friedel-Crafts acylation of butyl phenyl ether (**8**) was also studied. The acylation of **8** with $AlCl_3$ as catalyst cleanly afforded the *para* product (**9**). However, when $AgClO_4$ and a base were used, the reaction afforded approximately 7% of the *ortho* product (**10**).

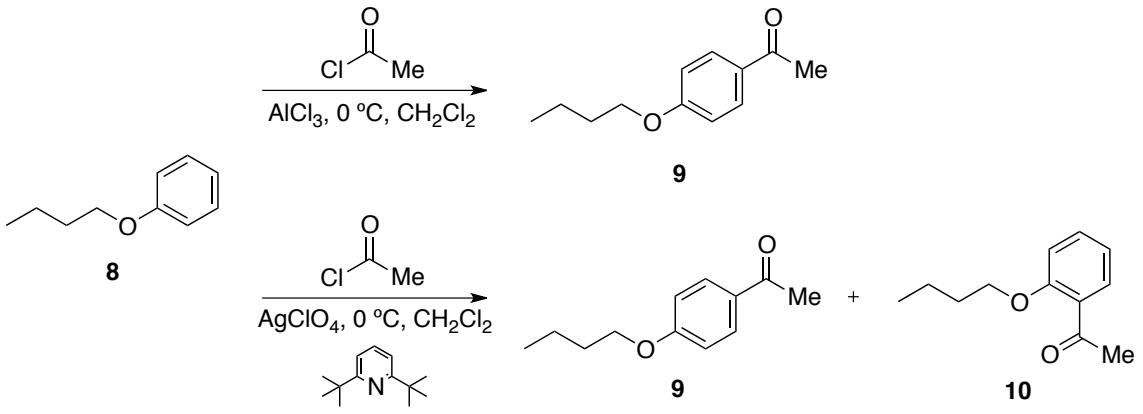


Figure 3 - 4: Acylation reactions of butyl phenyl ether used to aid in the mechanistic understanding of veratrole reactions

Intermolecular ^{13}C KIEs. Intermolecular KIEs are the measure of the impact of isotopic substitution on the overall reactivity of a molecule, reflecting the transition state for the rate-limiting step of the reaction.[116] The intermolecular ^{13}C KIEs for the Friedel-Crafts acylation of veratrole were determined combinatorially at natural abundance by NMR methodology. Two independent acylations of veratrole mediated by $AgClO_4$ / 2,6-di-tert-butylpyridine at 0 ºC in CH_2Cl_2 were taken to 70 ± 2% and 68 ± 2% convertion, the unreacted veratrole was recovered by an aqueous workup followed by column chromatography. The recovered veratrole was then analyzed by ^{13}C NMR by comparison with a standard sample of veratrole that was taken from the same reagent bottle. The relative changes in ^{13}C isotopic composition in the aromatic carbons were determined using the methoxy carbons as an internal standard with the assumption that their isotopic composition did not change during the reaction. From the changes in isotopic composition of the aromatic carbons, the ^{13}C KIEs were calculated as previously described.[34] An analogous process was used to measure the ^{13}C KIEs for the acylation of veratrol using $AlBr_3$, and for butyl phenyl ether.

The KIEs found for the acylation of veratrole catalyzed by $AgClO_4$ are shown in Figure 3 - 5a. An important observation about these KIEs is that they are quite small for positions expected to exhibit a primary isotope effect, but it should be recognized that the observed isotope effects for the symmetrical veratrole are necessarily an average of the individual isotope effects at the C4 and C5 positions. For an unsymmetrical electrophilic attack, the carbon being attack would be expected to have a very small isotope effect that would be averaged with that for the carbon being attacked, lowering

the overall KIE observed. These results qualitatively suggest that the rate-limiting step of this process is the carbon-carbon bond formation to obtain the σ-complex. Which is expected based on the conventional mechanistic explanation of this reaction. A quantitative meaning of these isotope effects will be discussed later.

On the other hand, the KIEs obtained from the acylation of veratrole using $AlBr_3$ suggest a different story (Figure 3 - 5b). In this case the most important observation is that the KIEs for the aromatic carbons are all very small, essentially within experimental error of unity. These unusual KIEs were also found for the acylation of butyl phenyl ether, at 0 ºC with $AlCl_3$ as catalyst (Figure 3 - 5d). The qualitative interpretation of these results is that the rate-limiting transition state involves little or no bonding of the electrophile to the aromatic carbons. In order for the electrophilic attack to be rate-limiting, the transition state would have to be very early. In these cases the isotope effects could be considered reasonably consistent with rate-limiting diffusional encounter of the electrophile.

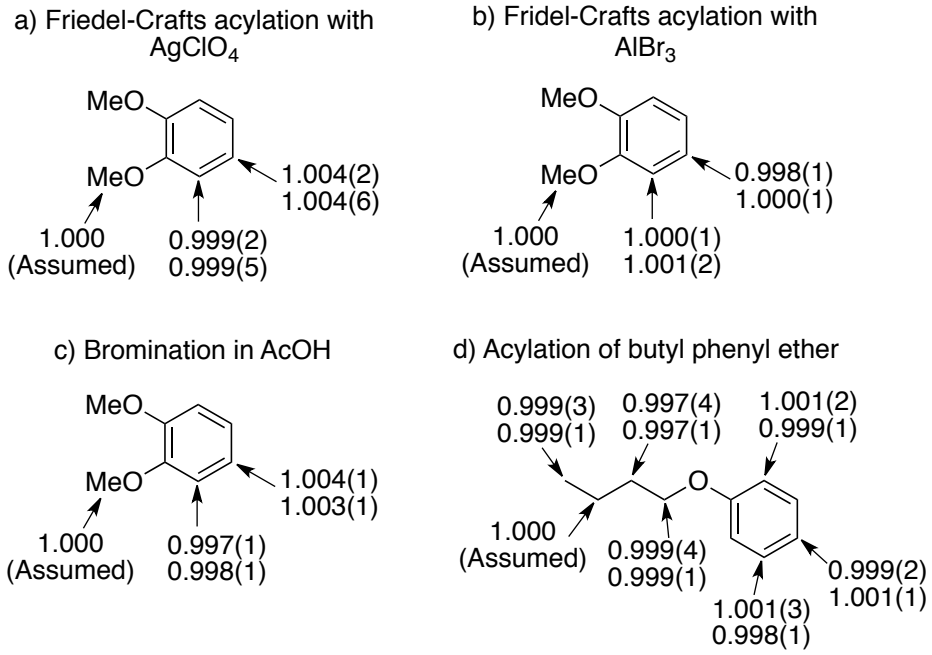


Figure 3 - 5: Intermolecular ^{13}C KIEs (k_{12}/k_{13}) for electrophilic aromatic substitution reactions. (a) Friedel-Crafts acylation of veratrole using acetyl chloride / $AgClO_4$ / 2,6-di-tert-butylpyridine in CH_2Cl_2 at 0 ºC. (b) Friedel-Crafts acylation of veratrole using acetyl chloride / $AlBr_3$ in CH_2Cl_2 at 25 ºC. (c) Bromination of veratrole using Br_2 in acetic acid at 0 ºC. (d) Friedel-Crafts acylation of butyl phenyl ether using acetyl chloride / $AlCl_3$ in CH_2Cl_2 at 0 ºC.

In order to obtain KIEs for the bromination in acetic acid, reactions of natural-abundance veratrole were taken to 77 ± 2% and 74 ± 3% conversion using limiting bromide at 0 ºC, and the unreacted veratrole was recovered by removing most of the acetic acid under vacuum, followed by an aqueous workup and fractional distillation. NMR analysis, as described before, led to the isotope effect shown in Figure 3 - 5c. The KIEs of 1.003-1.004 at C4 / C5 are similar to the isotope effects found for the acylation mediated by $AgClO_4$. Overall, the C4 / C5 KIE, while small, is qualitatively consistent with a rate-limiting electrophilic attack on one of these carbons. A more quantitative

interpretation of these KIEs will be possible later with the help of theoretically calculated isotope effects.

Intramolecular KIEs. Intramolecular KIEs reflect the relative facility of two branches of a mechanism that are equivalent, except for isotopic substitution. This means that they characterize the first irreversible step undertaken by an initially symmetrical molecule after losing symmetry on the path to product formation, we will refer to this step as the 'product-determining step'.

The intramolecular ^{13}C KIEs at C4 / C5 for acylation of veratrole were determined from analysis of samples of product **6** (for both reaction conditions), using methodology for the accurate and precise measurement of the relative integrations of pairs of peaks within a spectrum.[105, 117-118] This methodology includes high digital resolution, long delays, centering the peaks of interest within the spectral window, and integration ranges that are a constant multiple of the peak width at half height. A complication in the numerical interpretation of these integrations is that C4 is subject to three ^{1}J ^{13}C-^{13}C couplings with satellites not included in the integration range, while C5 is only subject to two such satellite couplings. To allow for this, the integrations at C4 were adjusted by the 0.0107(8) natural abundance of ^{13}C. The results obtained after this correction are shown in Figure 3 - 6a and b.

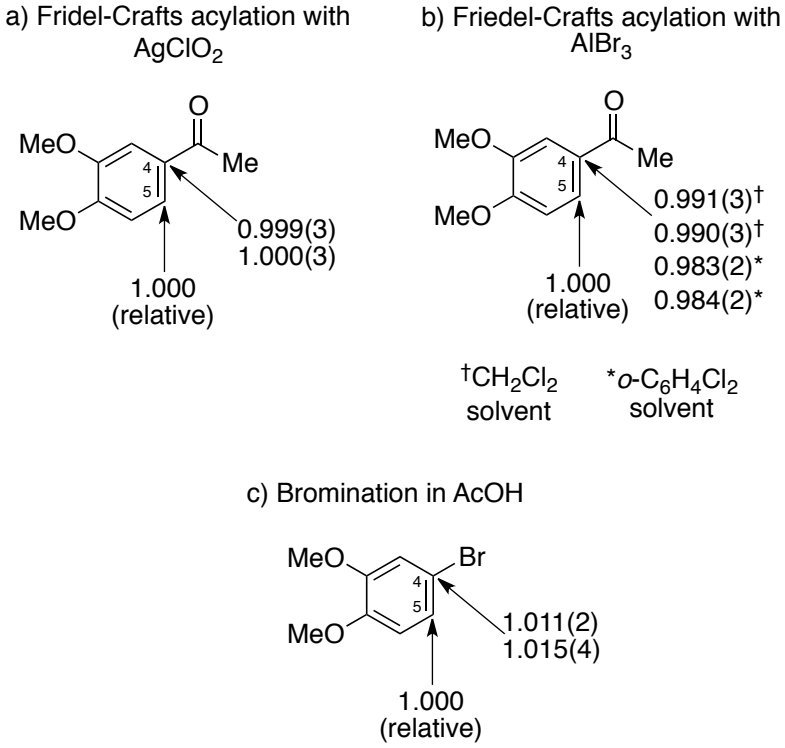


Figure 3 - 6: Intramolecular ^{13}C KIEs, defined as (^{12}k / ^{13}k *at C4*) / (^{12}k / ^{13}k *at C5*), for electrophilic aromatic substitution reactions. (a) Friedel-Crafts acylation of veratrole using acetyl chloride / $AgClO_4$ / 2,5-diterbutyl pyridine in CH_2Cl_2 at 0 ºC. (b) Friedel-Crafts acylation of veratrole using acetyl chloride / $AlBr_3$ in CH_2Cl_2 or *o*-dichlorobenzene at 25 ºC. (c) Bromination of veratrole using Br_2 in acetic acid at 0 ºC.

Interestingly, the acylation of veratrole mediated by $AgClO_4$ showed no significant KIE for the formation of this carbon-carbon bond (Figure 3 - 6a). In addition, the Friedel-Crafts acylation of veratrole using $AlBr_3$, with both solvents, showed a substantial *inverse* KIE (Figure 3 - 6b). In this case, the solvent used appears to have a small effect on the reaction – KIE seems to be slightly more inverse in *o*-dichlorobenzene. Both of these results are highly unusual and are opposite to what would be expected from a reaction involving a carbon-carbon bond formation at C4.

For comparison, the intramolecular ^{13}C KIE at C4 / C5 for bromination of veratrole in acetic acid was determined by analysis of **7** obtained from reactions taken to 91-93% conversion. (No detectable dibromination product was observed in these reactions.) In this case, the ^{13}C composition in the brominated C4 was less that in the C5 position. This isotopic composition corresponded to intramolecular KIEs, defined as with **6**, of 1.011-1.015 (Figure 3 - 6c). The normal isotope effect for bromination fits with the qualitative expectations for a product-determining transition state involving the formation of a carbon-bromine bond.

H/D KIEs. In some electrophilic aromatic substitution reactions, loss of a proton from the intermediate σ-complex can be fully or partially rate limiting. This includes Friedel-Crafts acylation reactions under some conditions.[119-120] Rate-limiting deprotonation of the σ-complex would still not account for the observed isotope effects for either of the acylations, as a normal ^{13}C KIE would be expected for the deprotonation step. However, it was important to evaluate this potential complication.

For this reason, the H/D KIEs were studied for veratrole. Veratrole-d_4 was prepared by successive exchange reactions at ≈100 °C with D_2O / H_2SO_4 followed by D_2O / D_2SO_4, and was found to be 98.6% deuterated in the aromatic positions based on NMR analysis. Acylations using $AlBr_3$ of 1:1 mixtures of veratrole-d_4 and veratrole-d_0 taken to 7% and 6% conversion (limited by rapid quenching with an excess of an aqueous bicarbonate solution) afforded in both cases a 1.01 : 1 ratio of **6** : **6**-d_3 by NMR analysis (using 21.6 s delays, ≈5 x T_1, between p/2 pulses). Mass spectral analysis of recovered veratrole from each reaction revealed that negligible H / D exchange had

occurred in the starting material under these conditions. The k_H/k_D of 1.01 (± ≈5%) rules out rate-limiting deprotonation of the σ-complex.

Computational Studies

A. The energy surface for addition of acetylium cation to veratrole. The application of theoretical calculations to mechanistic studies of electrophilic aromatic substitution represents a substantial challenge due to the importance of charge-separated species in the mechanistic pathway. To mitigate this problem, the calculational models here employ a variety of approaches. Initially, we avoid the issue of zwitterionic charge separation by looking at cationic species in the absence of a counterion, including implicit or explicit solvent models. We then include a counterion along with implicit or explicit solvent. Ultimately, it is questionable whether any practical theoretical model can adequately and reliably represent the energy surface for the reaction in solution. Instead, our goal was to computationally explore mechanistic models against which our unusual experimental observations can be interpreted.

The computational studies to be described here include B3LYP/6-31G*, B3LYP/6-31+G**, M06-2X/6-31+G**, and MP2/6-31+G** calculations. The B3LYP calculations were employed most broadly. The other calculations were employed selectively to determine whether the choice of method leads to any qualitative differences in the results. Because B3LYP calculations are subject to particular inaccuracies in the energetics of reactions that convert π-bonds to σ-bonds, the energetically more balanced M06-2X calculations were employed as a particular check

in cases where this error was potentially relevant. In no case was there a qualitatively important difference in the predictions of the methods.

In gas-phase B3LYP/6-31+G** calculations, the addition of acetylium cation (**11**) to C4 / C5 of veratrole to afford **12** is downhill by 31.5 kcal/mol (pot. E + zpe) and there is no potential energy barrier for the reaction. Solvent will tend to preferentially stabilize the more localized charge of **11** over the delocalized charge of **12**, but **12** is still downhill from **11** + veratrole by 11.9 kcal/mol (B3LYP/6-31+G**/PCM + zpe with full geometry optimization) when a PCM solvent model for CH_2Cl_2 is employed. This exothermicity is in contrast to the conventional picture that leads to the expectation of a late transition state.

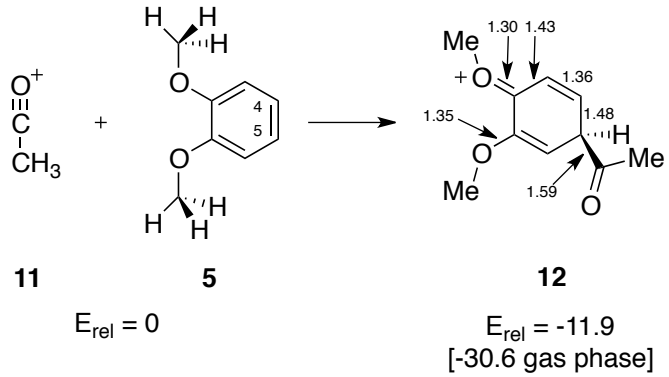


Figure 3 - 7: Relative energy for the reaction of acetylium ion with veratrole to afford the σ-complex **12**

Relaxed energy surfaces for approach of **11** to veratrole were explored by fixing the Cα-C4 and Cα-C5 distances at a grid of values and optimizing the remaining geometrical variables at each point. The B3LYP/6-31+G**/PCM + zpe surface generated in this way is shown in Figure 3 - 8. Similar surfaces were obtained in M06-2X/6-31+G** and MP2/6-31+G** calculations in both the gas phase and with a solvent model (though the gas-phase surface is more sloping due to the greater exothermicity in the gas phase). The essential feature of each of these surfaces is that the preferred approach of **11** is symmetrical between C4 and C5 at long Cα-C4/C5 distances. As **11** comes closer to the veratrole, its approach ultimately breaks symmetry to afford the chiral **12**, but the symmetry breaking is not favored until the Cα-C4/C5 distances are less than 2.8 Å.

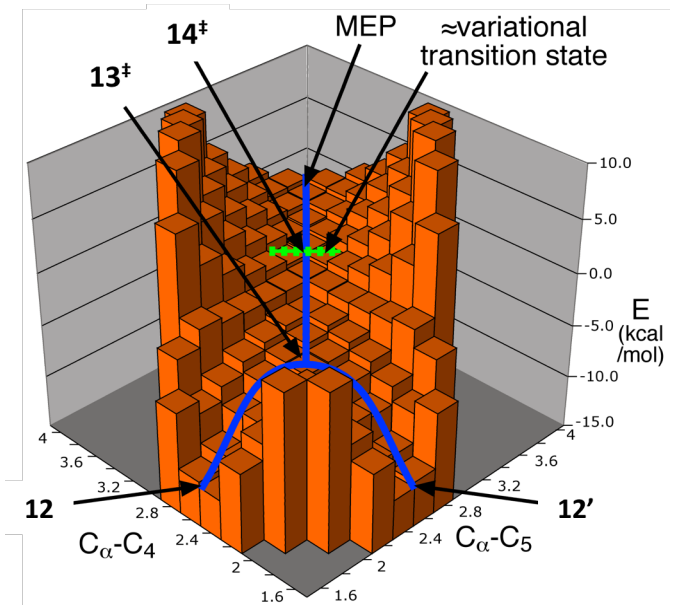
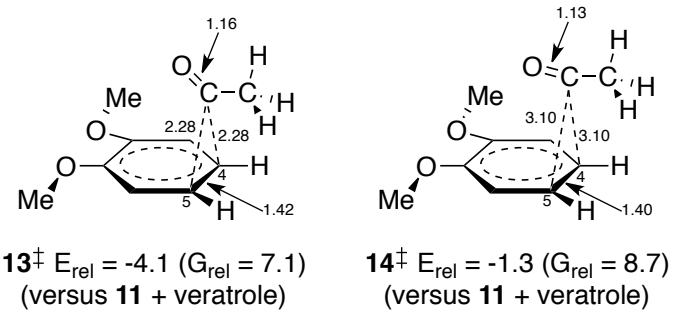


Figure 3 - 8: Energy surface (B3LYP/6-31+G**/PCM + zpe) for the approach of acetylium ion **11** to veratrole, fixing Cα-C5 distances at the values apecified on the grid. Higher-energy points at the left, right, and front of the grid have been left out for clarity.

In more technical detail, the reaction's minimum-energy path (MEP, the steepest-descent path in mass-weighted coordinates starting from a geometry with Cα-C4 and Cα-C5 distances of 3.95 Å) passes through a C_s-symmetric channel in which modes orthogonal to the MEP all have a positive curvature. The MEP then passes a valley-ridge inflection point (VRI) when Cα-C4 = Cα-C5 ≈ 2.8 Å, at which point one of the modes has a zero curvature. At shorter distances, an orthogonal mode involving side-to-side motion of the acetylium ion has a negative curvature, and real trajectories will tend to diverge from the MEP. The MEP itself can only bifurcate at a stationary point, and it proceeds to saddle point **13**‡, the transition structure for a 1,2-migration of the acyl group equilibrating **12** and its enantiomer **12'**.



13‡ E_{rel} = -4.1 (G_{rel} = 7.1) (versus **11** + veratrole)

14‡ E_{rel} = -1.3 (G_{rel} = 8.7) (versus **11** + veratrole)

Figure 3 - 9: Transition states for the symmetrical approach of the acetylium ion to C4 / C5 veratrole at different distances.

Within this computational model, the addition of acetylium cation to veratrole has no meaningful conventional transition state. Under these circumstances, it becomes necessary to analyze the reaction within the context of canonical variational transition state theory (VTST). The canonical variational transition state (VTS) is then the dividing surface between the starting materials and the product at which the free energy is a maximum. The location of the VTS can be approximated from entropy estimates based on the unscaled harmonic frequencies. This is problematical due to the inaccuracy of such entropy estimates for loose structures, but following the MEP the free energy reaches an approximate plateau centered on structure **14**‡ with a Cα-C4 / Cα-C5 distance of 3.1 Å. Another way to estimate the position of the VTS, without the limitations of the harmonic approximation and frequency calculations on weak complexes, is to start trajectories at differing geometries and examine their outcomes. As discussed below, trajectories started at a Cα-C4 / Cα-C5 distance of 3.1 Å invariably formed the product

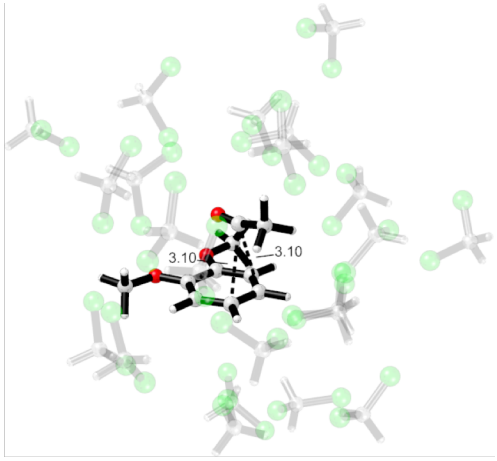
σ-complex. However, trajectories started at a distance of 3.4 Å only formed the σ-complex 39% of the time. This suggests that the actual VTS is closer than 3.4 Å.

B. Addition in the presence of explicit solvent. The real reaction could be complicated by the presence of solvent molecules in ways that implicit solvent models cannot account for. For example, assuming that **11** approaches the veratrole symmetrically, the arrangement of solvent molecules surrounding the reactants as the approach progresses will in any individual case be unsymmetrical. It might be envisioned that the arrangement of solvent molecules could dictate whether **12** or **12'** is formed. This would be important because if the solvent asymmetry predetermines which σ-complex is formed, there would be no opportunity for selectivity (including intramolecular isotope effects) to arise on the bifurcating surface. In addition, the preference for symmetrical approach could conceivably be lost if explicit solvent best stabilized an unsymmetrical approach. Finally, solvent could certainly affect the position of the VTS, and an unsymmetrical transition state would be anticipated if the transition state is sufficiently late.

These issues were studied applying two different computational models (Figure 3 - 10). The simplistic "Model-22" calculations included 22 explicit CH_2Cl_2 molecules in ONIOM, using a B3LYP/6-31G* layer for the **11** + veratrole and using an AM1 layer for the CH_2Cl_2 molecules. The more rigorous but less versatile "Model-66" used 66 explicit CH_2Cl_2 in an ONIOM using M06-2X/6-31G* for the reaction core and a PM3 layer for the CH_2Cl_2 molecules. An advantage of Model-22 is that it was simple enough to allow location of optimized structures on the energy surface. Low-energy solvent

configurations in the area of the energy surface for attack of **11** on veratrole were obtained by repeated cycles of simulated annealing with a maximum temperature of 600 K and confining the molecules to a 14 Å cubic box, fixing the Cα-C4 / Cα-C5 distances at 3.1 Å. Of the structures found, **15** was the lowest in energy. (The limited annealing process is unlikely to have found the global minimum, and it would not be particularly meaningful if it had.) Structure **15** was then used to calculate predicted isotope effects as described below.

a)



15

b)

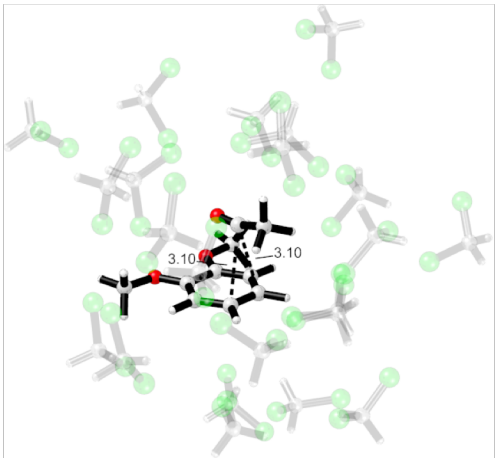


Figure 3 - 10: Structures including explicit solvent. (a) Structure **15**, an optimized structure obtained using Model-22 (see text) with fixed Cα-C4 / Cα-C5 distances of 3.1 Å. (b) An example starting geometry for trajectories using Model-66. In both structures the solvent molecules are partially transparent and obscured when in front of the solute.

Using Model-66, a starting structure was first generated in fully PM3 dynamics calculation, confining the molecules to a 19.8 Å cubic box, fixing the Cα-C4 / Cα-C5 distances at 3.1 Å, and following a simulated annealing cycle at 600 K with a 10 ps equilibration at 25 °C. The ONIOM was then employed and the model was equilibrated

for 2 ps in fully classical direct dynamic trajectories.[121-123] At 250 fs intervals for 6.5 ps, points and velocities were extracted and the fixed atoms were given Boltzmann-random velocities for 25 °C. The trajectories were then followed forward and backward in time employing a Verlet algorithm and using 1-fs steps. In each of 25 trajectories, both ends of the trajectory afforded **12** or **12**' within 800 fs, with a median time of 153 fs. This strongly suggests that the VTS for attack of the acetylium ion on veratrole is outside of the 3.1 Å interatomic distance. In these trajectories, the same product formed 23 times and differing products were formed 12 times. This preference would happen by chance only 5% of the time. The result suggests that the solvent orientation does influence the positional selectivity to some degree while not completely preordaining it, allowing the selectivity to be influenced by small factors such as isotopic substitution.

Further information can be obtained from examining the time-course of the Cα-C4 and Cα-C5 distances for these trajectories (Figure 3 - 11). The key observation is that the trajectories proceed through a relatively narrow swath and do not segregate into separate channels for the formation of **12** versus **12'** until late in the trajectory, after the Cα-C4 or Cα-C5 distance has closed to less than 2.4 Å. The initial course of the Cα-C4 versus Cα-C5 distances does not predetermine the final product – many trajectories approach along a middle axis between **12** and **12'**. In sum, the trajectories including explicit solvent are consistent with the expectation from the bifurcating energy surface in Figure 3 - 8 of product selectivity being decided on the downward slope of an energy surface, after the rate-limiting transition state.

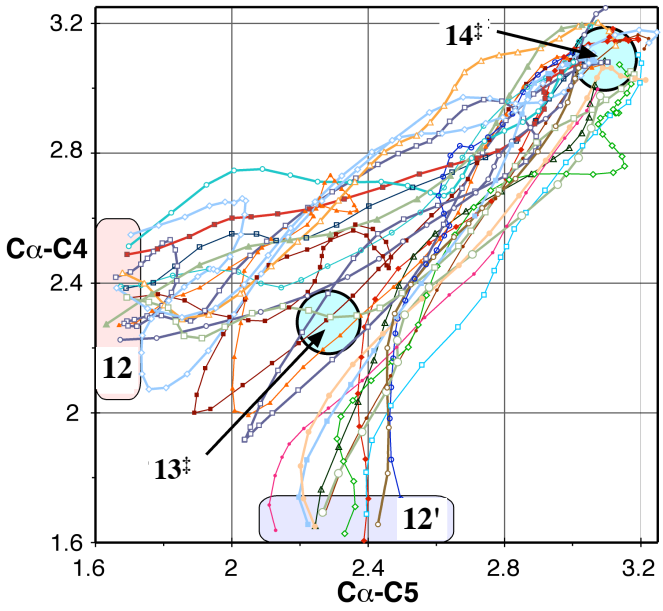
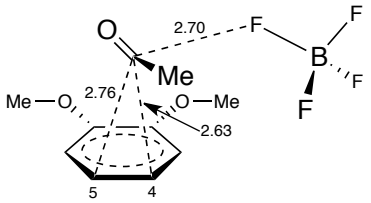


Figure 3 - 11: Time-course of Cα-C4 and Cα-C5 distances for trajectories started from **14**‡ in explicit CH_2Cl_2. Markers are placed at 5 fs intervals.

C. Addition including the counterion. The $AlBr_3Cl^-$ counterion involved in our experimental reactions was computationally modeled here for simplicity as BF_4^-, assuming that the choice of the counterion would not qualitatively affect the mechanism. In B3LYP/6-31+G**/PCM calculations, transition structure **16**‡ was located for the reaction of veratrole with an acetylium BF_4^- ion pair. Unlike the reaction in the absence of counterion, the reaction including the counterion faces a conventional potential energy barrier. With Cα-C4 at 2.67 Å, the transition structure is still early with respect to carbon-carbon bond formation. A notable feature of **16**‡ is that the counterion has imparted asymmetry to the approach of the acetylium ion to the veratrole – the Cα-C4 or Cα-C5 distances are now unequal. Using **16**‡ as the starting point for an IRC, we found that it leads to the attack at C4, forming **12'**. This provides no information about whether

trajectories passing through **16**‡ could also lead to attack at C5, giving **12**. As discussed above for asymmetry imparted by the solvent, an important question is whether the transition state can lead to both **12** and **12'**, allowing the selectivity necessary for the intramolecular KIE to not be congruent with the intermolecular KIE. Quasiclassical trajectories started from **16**‡ are ambivalent on this issue. Out of 25 trajectories, 21 afforded **12'** and 4 afforded **12**. These results suggest that a tightly-bound counterion would bias the attack strongly. If so, the observed intramolecular KIE would be dictated by the KIE for **16**‡ itself. This is qualitatively inconsistent with the experimental observations, and the inconsistency will be supported quantitatively in the next section.



16‡ E_{rel} = -0.4 (G_{rel} = 11.6)

Figure 3 - 12: Transition state for the addition of the acetylium ion including the counter ion.

Should the counterion be so tightly associated at the transition state? While structure **16**‡ is a saddle point on the potential energy surface, entropy will also affect the distance between the loosely coordinated counterion and the acetylium ion as the attack on veratrole proceeds. To gauge qualitatively the effect of entropy on the looseness of

the counterion association, classical trajectories were initiated from **16**‡ at 25 °C, fixing the Cα-C4 or Cα-C5 distances but leaving all other motions variable. When this is done, the BF_4^- ion traverses its potential energy well over time in a way that reflects both the potential energy and the classical entropy. The average distance between Cα and the nearest fluorine atom over a series of four 1-ps trajectories was 3.22 Å. This implies that the counterion association as the acetylium ion approaches the veratrole is likely much looser than suggested by **16**‡. This will tend to decrease the approach asymmetry induced by the counterion. Ultimately, the experimental intermolecular and intramolecular ^{13}C KIEs in the acylation [Figures 3 – 5 (a and b) and 3 – 6(a and b)] by themselves rule out the importance of the tightly-bound ion pair **16**‡ to the experimental mechanism.

For acylations of moderately reactive aromatics such as benzene and toluene mediated by acetyl chloride / $AlCl_3$, there is considerable evidence that the reactive electrophile is an acylium ion / counteranion ion pair. For example the toluene / benzene rate ratio is 128 using acetyl chloride / $AlCl_3$ and 125 when using the preformed acetylium salt $CH_3CO^+SbF_6^-$.[119-120, 124] For more reactive aromatics such as anisole, however, it has at times been proposed that the reactive electrophile is an acetyl chloride / $AlCl_3$ complex with the aluminum complexed at oxygen, **17**.[125-126] The simplest evidence for their direct involvement in the mechanism comes from acylium ion decomposition reactions that are inhibited in the presence of highly reactive aromatics, though this inhibition could result from a simple decrease in the lifetime of intermediate acylium ions rather than a change in mechanism.

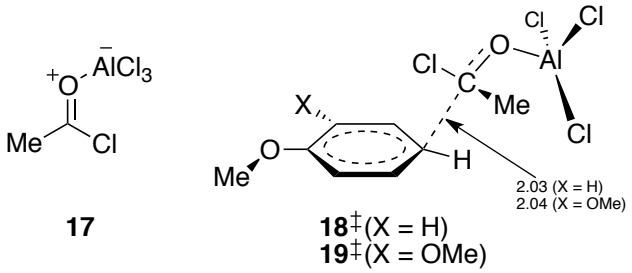


Figure 3 - 13: Transition states for the reaction of **17** with veratrole and anisol

In order to test this issue for the acylations studied here, transition structures **18**‡ and **19**‡ were located using B3LYP/6-31+G**/PCM calculations for the direct reaction of **17** with anisole and veratrole, respectively. This direct mechanism was then assessed by the comparison of predicted KIEs based on **18**‡ and **19**‡ with the experimental KIEs, as described in the next section.

Predicted isotope effects. To evaluate the consistency of various mechanistic possibilities with the observed isotope effects, ^{13}C KIEs or equilibrium isotope effects were predicted for a series of structures. These predictions were carried out by the method of Bigeleisen and Mayer[41, 127] using the scaled theoretical vibrational frequencies.[128] For KIEs, tunneling corrections were applied using a one-dimensional infinite parabolic barrier model.[129] Such KIE predictions including a one-dimensional tunneling correction have proven highly accurate in reactions not involving hydrogen transfer, so long as the calculation accurately depicts the mechanism and transition state geometry.[29, 130-132]

The small intermolecular ^{13}C KIEs obtained for the acylation of veratrole using $AgClO_4$ are consistent with a rate-limiting carbon-carbon bond formation, and small enough to suggest the involvement of an early transition state. In addition, the negligible intermolecular KIEs for the acylation using $AlBr_3$ as the catalyst are consistent with either a very early transition state for electrophilic attack or rate-limiting diffusional encounter of the electrophile. It is important to notice that, in either case, the KIEs are not consistent with the conventional picture of a late transition state. For example, a large KIE of 1.023 is predicted (Figure 3 - 14a) for the carbon being attacked in transition structure **20**‡ (B3LYP/6-31+G**/PCM) for the acylation of benzene. Also, large KIEs are predicted from the late transition states **18**‡ and **19**‡ associated with direct reactions of complex **17**. With veratrole the predicted KIE is mitigated by averaging of the KIEs for reactive / unreactive C4 / C5 centers, leading to a predicted KIE of 1.014. With anisole there is no issue of averaging and the predicted KIE based on **18**‡ is 1.029. In either case the discrepancy between the predicted and experimental KIEs is compelling evidence against the importance of direct reaction with **17** in these reactions.

The predicted intermolecular KIE of 1.006 for C4 / C5 in the ion-pair transition structure **16**‡ (Figure 3 - 14b) is very close to the experimental value obtained for the acylation of veratrole using $AgClO_4$. However it is still too high when compared to the KIEs obtained when $AlBr_3$ was used. The predicted intramolecular KIE C4 / C5 in **16**‡ is also 1.006, which is too high compared to the experimental values obtained for both reaction conditions. These results suggest that the actual transition state involved in these reactions is earlier than **16**‡ and with the counterion not tightly bound, this inference fits

with the early VTS **14**‡ and the trajectory results with **15** and **16**‡. Structure **15** was used as a starting material reference structure, and used to predict isotope effects. The structure consists of a veratrole molecule surrounded by 22 explicit CH_2Cl_2 molecules, minimized in an ONIOM calculation. The resulting isotope effects are negligible and fit well with the experimental KIEs obtained from the acylation using $AlBr_3$. This observation provides no special support for the relevance of **15**, as any structure with the acetylium ion and veratrole sufficiently separated would likely lead to a similar prediction.

The prediction of the isotope effects for **14**‡ is complicated. There is little change in the relative zero-point energies for the carbons of the veratrole moiety of **14**‡ versus free veratrole, so that the isotope effects calculated from the reduced isotopic partition functions of the two are negligible (Figure 3 - 14b). However, the Bigeleisen formalism for predicting isotope effects also includes a factor for the ratio of the imaginary frequencies for light versus heavy atoms. This factor may be viewed as representing a relative entropy change for light versus heavy atoms in going from the starting materials to the transition state due to the loss of the entropy associated with the transition vector. The imaginary frequency factor is very important for the correct prediction of isotope effects.[29, 130-132] In this case, it lead to the prediction of substantial relative isotope effects at C4 / C5 (≈1.006) versus the methoxy carbons, even when the acetylium ion is placed 6.0 Å away from C4 / C5. This prediction matches well with the intermolecular isotope effects found for the acylation of veratrole (**5**) mediated by $AgClO_4$. These results are consistent with a mechanism that involves the rate-limiting formation of a carbon-carbon

bond. But, it does not explain the experimental results obtained for the acylation mediated by $AlBr_3$. In a similar fashion, the approach of an acetylium ion to **8** leads to predicted KIEs at the *para* carbon of 1.008. However, neither **5** nor **8** exhibit *any* detectable ^{13}C KIE at their reactive positions when the acylation is done using $AlBr_3$ or $AlCl_3$, respectively. The difference here between theory and experiment requires either a mechanistic explanation (such as encounter-controlled reaction) or an error in the physical model for calculating the KIEs. An argument for the latter is that the molecular rotation associated with the transition vector in the gas-phase-like calculation of $\mathbf{14}^{\ddagger}$ should not be applicable to the solution reaction where solvent-molecule motion is also heavily involved. This *ad hoc* idea is not very satisfying but it is supported by the low predicted KIEs for **15**. Excluding this rotation, the isotope effects predicted for **14** match well with the acylation mediated by $AlBr_3$. This would presumably be true for any sufficiently early transition structure.

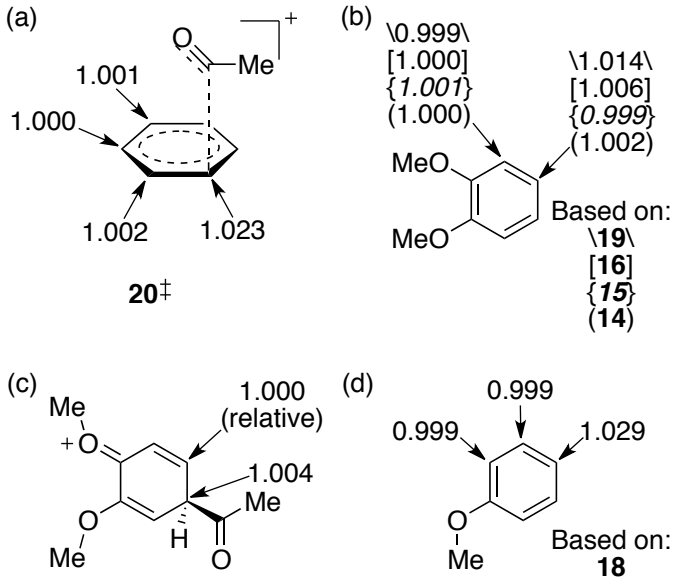
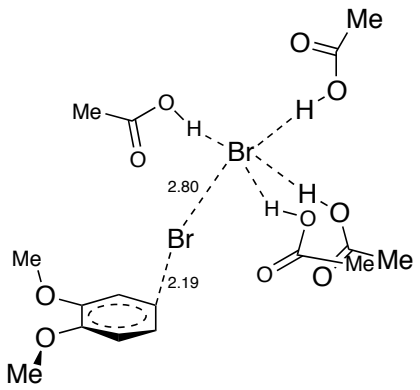


Figure 3 - 14: Predicted isotope effects at 25 °C for various mechanistic models for acylation. (a) Predicted ^{13}C KIEs (k_{12}/k_{13}) for acylation of benzene based on the B3LYP/6-31+G**/PCM transition structure **20**‡. (b) Predicted ^{13}C KIEs based on transition structures **14**‡, **15**, and **16**‡. The KIEs for **14**‡ are calculated from the reduced isotopic partition functions for **14**‡ versus veratrole. The KIEs predicted for C4 / C5 of veratrole notably reflect an average of the KIEs for the two positions. (c) Predicted relative ^{13}C equilibrium isotope effects (K_{12}/K_{13}) for equilibration of **12** and **12'**. (d) Predicted ^{13}C KIEs based on transition structure **18**.

We were able to predict the intramolecular isotope effects observed for the acylation of veratrole using $AgClO_2$. In this case, a sufficiently early transition state with the counter ion not tightly bound, like VTS **14**‡, will explain the experimental results. This prediction suggests that a symmetrical approach of **11** to veratrole via an early transition state will favor a bifurcating energy surface that will lead to the observation of a very small intramolecular KIE, essentially of a unity. On the other hand, the prediction of the unusual intramolecular ^{13}C KIE at C4 / C5 for the acylation of veratrole using $AlBr_3$ was not achievable using any conventional mechanistic model. We considered the

possibility that the final disposition of the acetylium group was determined by an equilibration of **12** and **12'** followed by a product-determining step, presumably loss of a proton. However, the relative equilibrium isotope effect in **12** is such that it favors ^{12}C in the substituted position and ^{13}C in the unsubstituted position (Figure 3 - 14c), contrary to experiment. In a transition state for removal of a proton from **12**, the preference for the lighter isotope at the carbon losing the proton would be expected to increase, so the KIE would be even further from the experimental values.

The prediction of isotope effects for the bromination of veratrole in acetic acid required a model for the bromination transition state. Solvent-model calculations in the absence of explicit solvent were inadequate for this task, as the formation of a σ-complex / bromide ion pair from veratrole / Br_2 is monotonically uphill with no saddle point in B3LYP/PCM calculations. With the inclusion of four explicit acetic acid molecules, transition structure **21**‡ was located in B3LYP/6-31G*/PCM calculations Figure 3 – 15). It should be emphasized that the real reaction in solution would involve an ensemble of solvent arrangements, with **21**‡ having no particular significance. However, **21**‡ provides a model for the prediction of isotope effects.



21‡

Figure 3 - 15: Transition state for the bromination of veratrole using explicit acetic acid molecules.

The results are summarized in Figure 3 - 16. The predicted KIEs for bromination based on **21**‡ matched strikingly with the experimental values, and in fact they are in each case within the range of the experimental uncertainty. The suggestion from these results is that the basic features of **21**‡, as a late transition state committed to bromine substitution at a particular carbon, are reasonably representative of the ensemble of transition states occurring in solution.

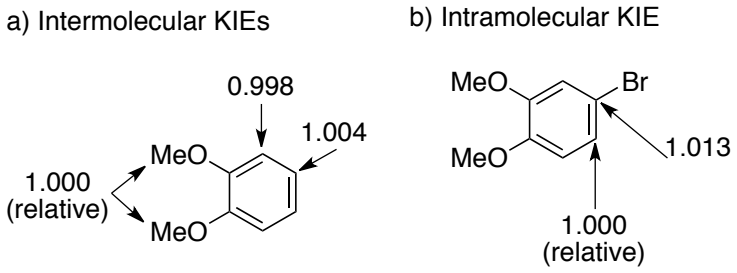


Figure 3 - 16: Predicted ^{13}C KIEs (k_{12}/k_{13}) at 25 °C for bromination based on **16**‡. (a) Predicted intermolecular KIEs, made relative to the methoxy groups for comparison with experiment. The average absolute predicted KIEs for the methoxy groups, C3 / C6 positions, and C4 / C5 positions are 1.002, 1.000, and 1.006, respectively. (b) The predicted intramolecular KIE.

Due to the energetic disadvantage of breaking aromaticity, most electrophilic aromatic substitutions involve a late transition state in the step forming a σ-complex. Late transition states afford no opportunity for dynamic control of the positional selectivity, so when σ-complex formation is rate limiting, the observed selectivity should correspond closely with the rate of the reaction. This correspondence is documented in the extensive observations of Brown.[91] The situation differs when a highly reactive arene is combined with a highly reactive electrophile. Now the transition state committing the reactants to form product is early. When sufficiently early, the positional selectivity for electrophilic attack may not yet be decided at the transition state. Our hypothesis is that the selectivity is then determined by dynamics on the downward slope toward σ-complex formation. If this idea is correct, a key problem becomes the identification of experimental observations that are indicative of dynamically determined selectivity.

It is first necessary to recognize when the rate-limiting step has separated from the product-determining "step". The conventional approach of testing the Brown selectivity relationship is arguably a blunt tool in this regard, both because of complications in its application[109] and because of the potential for false negatives if the selectivity expressed in the product-determining step resembles that expected for the rate-limiting step. The latter flaw should be borne in mind; much of the literature focus on reactivity / selectivity correlations that follow the Brown relationship ignores the one-sided nature of the evidence. Isotope effects provide a superior alternative because they reflect molecular geometries and so are unlikely to coincidentally match for separate steps along a pathway. Indeed, the comparison of intermolecular and intramolecular deuterium KIEs has long been used in elegant experiments to establish the separation of rate-limiting and product-determining steps.[133-134] Another advantage of isotope effects is that they are accurately theoretically predictable when controlled by transition states.

In the example of the bromination reaction, the correspondence of the intermolecular and intramolecular KIEs provides strong evidence for a single rate-limiting / product-determining step. The close correspondence of the two isotope effects is not obvious at first glance, because both the intramolecular KIEs (in general) and intermolecular KIEs (as measured here) are *relative* to differing standard carbons. In addition, the observed intermolecular KIEs are complicated by the averaging of KIEs at reactive and unreactive positions in the symmetrical veratrole. However, the KIEs are readily interpreted with the aid of theoretical calculations, and the highly accurate

prediction of both the intermolecular and intramolecular KIEs from the single transition structure **21**‡ strongly supports the conventional mechanism.

A quite different story is told by the KIEs for the acylation reactions. In these cases the intermolecular KIEs cannot be reconciled with the intramolecular KIEs. *This is unambiguous evidence for separate rate-limiting and product-determining steps*. What is the nature of these steps? A viable mechanism must account for the intriguing and unusual intramolecular KIEs. It does not appear that any conventional mechanism can do so. The question becomes whether dynamically determined selectivity on a bifurcating surface can account for this isotope effect. In principle, a count of the outcome of trajectories could be used to predict the intramolecular KIE, and we have previously developed specialized ways of predicting small isotope effects using trajectories employing super-heavy isotopes.[19, 71]

In the case of the acylation of veratrole mediated by $AgClO_4$ we found a small (due to the symmetry of the molecule) but significant intermolecular KIE at the C4 / C5 positions. On the other hand, we did not observed any significant intramolecular KIE at these positions. The intermolecular KIEs are unambiguous evidence that the rate-limiting step involves a carbon-carbon bond formation. In addition, we were able to predict and explain the origin of these KIEs. Interestingly, the inter- and intramolecular KIEs do not reconcile, suggesting that there has to be a product-determining step. However, our results can be explained using a VTS. In Figure 3 – 8 we showed the energy surface for the formation of **12** and **12'**. This surface describes how the symmetrical approach of **11** to the C4 and C5 of veratrole can lead to a bifurcating

energy surface. In this case, due to the symmetry of veratrole and the "early" nature of the transition state leading to the σ-complex formation, the acetylium ion can attack either of the two carbons (C4 or C5) preventing this way the observation of a significant relative isotope effect at these positions. Our results are clear evidence of the involvement of a bifurcating energy surface in the acylation of highly nucleophilic aromatics. In addition, they show that it is possible to have two kinetically-distinguishable steps with no intermediate.

On the other hand, for the acylation using $AlBr_3$ we found that there was no significant intermolecular KIEs at the C4 / C5 positions. These results suggest that the reaction of the acetylium ion with veratrole is governed by rate-limiting diffusional encounter of the electrophile. In addition, *inverse* intramolecular KIEs were observed under these conditions, for both solvents. In previous studies we were able to predict small KIEs with high precision. However, these cases involved neutral reactants in which gas-phase calculations were sufficient. Here, a PCM implicit solvent is not sufficiently realistic to model the charged reaction of an acetylium ion with veratrole, and reasonable models employing explicit solvent such as Model-66 cannot be applied to sufficient trajectories to make a KIE prediction. Attempts to apply the Lluch process[74] to the KIE prediction were unsuccessful because no dynamical bottleneck could be located.

In order to interpret these results, we decided to give a qualitative explanation by chemical analogy. In this regard, two examples seem relevant. The first case is the cycloaddition of dichloroketene with cis-2-butene (Figure 3 – 17). The results showed an

unusual inverse ^{13}C KIE was observed in that more ^{13}C was observed adjacent to the carbonyl carbon of the cyclobutanone product **22**.[19] Since this cycloaddition would be viewed as involving electrophilic attack of the carbonyl carbon of the dichloroketene on the olefinic carbons, it was expected that the carbonyl carbon would preferentially end up attached to ^{12}C, not ^{13}C. The second example is the singlet-oxygen ene reaction of tetramethylethylene (Figure 3 – 17). In this reaction, a preference was observed for the oxygen atom in the product **23** to be attached to a ^{13}C.[105] In both of these cases, other evidence supported the involvement of dynamics on bifurcating energy surfaces. In the case of **22** in particular, the observed KIE was accurately predictable from trajectories.

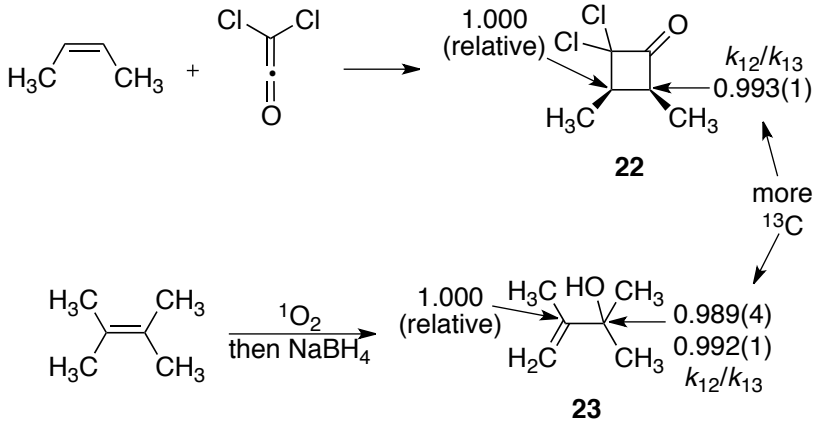


Figure 3 - 17: Examples of other reactions that showed inverse intramolecular isotope effects.

On a speculative level, these results suggest that the observation of an inverse intramolecular ^{13}C KIE in electrophilic additions to competing olefinic (or aromatic)

carbons is *characteristic* of selectivity on a bifurcating surface. The results for the acylation of veratrole might then be considered as the third example illustrating the trend and as indicative of the involvement of a bifurcating energy surface. A limitation on this ambitious interpretation is that chemistry at present simply does not understand selectivity on bifurcating surfaces enough to account for the trend or anticipate its limitations.

From a more conservative perspective, the prior results show that an inverse ^{13}C KIE is at least reasonably consistent with selectivity on a bifurcating surface. In the absence of any conventional alternative that accounts for the KIE, we conclude that the acylation of veratrole involves selectivity on a bifurcating surface. It is important to note that this conclusion can be reached prior to the consideration of the computational energy surface. The calculated surface of Figure 3 - 8 then supports the interpretation of the experimental results.

It is of interest to consider the physical origin of the bifurcating energy surface. At large intermolecular distances, the approach of an acetylium ion to veratrole should be dominated by electrostatic effects. In the electrostatic potential map of veratrole (Figure 3 - 18a), there are two regions of negative potential. The most negative of these surrounds the oxygen atoms, but this region is irrelevant to the subsequent chemistry. The second region is more interesting, as it is reached by a π-approach to the aromatic ring and its maximum is equidistant from C4 and C5. This shows that electrostatics thus favor a symmetrical approach. As the approach of the acetylium ion proceeds, the electrostatic energy effects are perturbed to greater and greater extents by frontier orbital

interactions. But here again, a symmetrical approach is initially favored because the HOMO of veratrole is a maximum along a plane splitting C4 and C5 (Figure 3 - 18b). As the approach continues, the energy of the system is ultimately dominated by product stability effects, favoring the unsymmetrical **13** over the transition state **14**‡. By this point, however, the VTS has already been crossed and the isotopic selectivity is determined by the dynamics on the downhill slope of the energy surface.

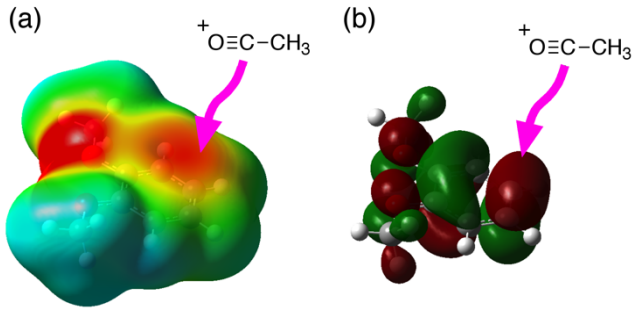


Figure 3 - 18: Electrostatic and orbital factors affecting the approach of an acetylium ion to veratrole. (a) An electrostatic potential energy map showing the negative region on π-approach to the aromatic ring. (b) The HOMO of veratrole. Both factors favor a symmetrical approach of the electrophile.

Two ideas here are key. The first is that a single transition state can lead to more than one σ-complex. The second is that substantial selectivity among σ-complexes is possible despite the barrierless nature of bifurcating surfaces. On this second point, phase-space theory importantly predicts that the ratio of the products from a bifurcating surface will be related to their relative stability,[75] and this idea fits with experimental

observations in other reactions involving bifurcating energy surfaces.[72] These concepts were not available during most of the history of the study of electrophilic aromatic substitutions. The symmetry breaking inherent in the surface of Figure 3 - 8 was at one time erroneously considered impossible as it would violate symmetry rules.[135] Because selectivity was viewed as requiring an intermediate, analyses long made the erroneous assumption that the absence of an intermediate would engender only statistical selectivity.[50]

These two ideas allow a unified qualitative understanding of the mechanism and selectivity of electrophilic aromatic substitution reactions. In Figure 3 - 19, the products *a* and *b* are regioisomeric σ-complexes, such as *para* versus *meta* adducts on a substituted benzene. We define the paths taken in reaching an isomer (*a* or *b*) as the average of all trajectories that form that isomer. Such paths would not be expected to diverge for *a* versus *b* until the electrophile approaches the arene sufficiently for the system to be influenced by the ultimately differing stabilities of the product σ-complexes. For the reaction of moderately reactive pairs of arene and electrophile, the formation of the σ-complexes is endothermic or thermoneutral (Figure 3 - 19a). The transition states are late and occur after the paths to *a* and *b* have diverged. The reactivity and selectivity are then both determined by the energies of the transition states leading to *a* and *b*, and the Brown selectivity relationship would hold.

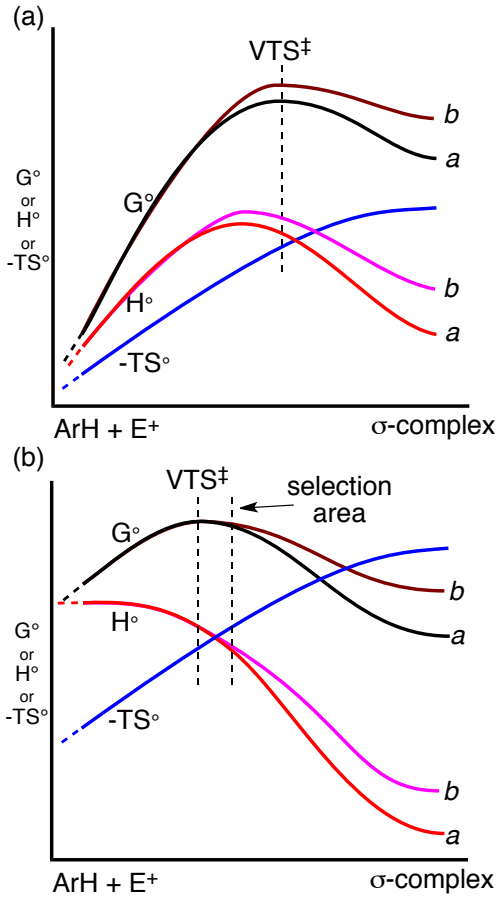


Figure 3 - 19: Generalized reaction coordinate diagram for electrophilic aromatic substitutions. (a) Moderately reactive arenes / electrophiles. (b) Highly reactive arenes /electrophiles. Products *a* and *b* are regioisomeric σ-complexes of differing stabilities.

For more highly reactive arenes and electrophiles, the addition would become exothermic and the transition state would move earlier. For sufficiently reactive addends, the enthalpic barrier for their bimolecular combination becomes small or disappears entirely (Figure 3 - 19b). This need not mean that the reaction becomes diffusion controlled; bimolecular reactions without enthalpic barriers may have rate constants far slower than diffusion due to entropic barriers.[136-145] It is thus possible to observe

substantial substrate selectivity in the absence of enthalpic barriers, and this is well recognized in the reactions of carbenes. The enthalpy curve still matters, even when the phenomenological barrier is entropic. Within VTST, the VTS would be reached when the downward slope of the enthalpy as the addends approach equals the upward slope of the – TS factor due to the loss of entropy as molecular degrees of freedom are restricted. Such transition states can be quite early, as in **13**‡, and occur prior to the divergence of the averaged paths to *a* versus *b*. The partitioning of trajectories into the *a*/*b* product valleys occurs in a "selection area" where the paths to the products diverge geometrically and energetically.[20] The selection area need not be widely separated from the VTS, and as noted above phase-space theory supports the influence of the product stability on the partitioning. Chemistry does not yet entirely understand the selectivity under these circumstances, but the separation of the selection area from the VTS only provides that the Brown selectivity relationship may fail, not that it must. It might be expected however that the selectivity relationship would be more likely to fail as the VTS and selection area become more separate, as should occur as the reaction becomes highly exothermic and the VTS moves earlier. In the other direction, as the reaction becomes less exothermic the reaction coordinate diagram of Figure 3 - 19b would morph into that of Figure 3 - 19a, with no need to postulate a discontinuity of experimental observations along the continuum.

Most importantly, there is no need to postulate an extra intermediate or two sequential barriers in order to account for experimental observations departing from the Brown selectivity relationship. Encounter complexes are involved in any bimolecular

reaction, and electrophile-arene π-complexes are surely present in many electrophilic aromatic substitutions. Nonetheless, intramolecular selectivity observations in no case require either to be kinetically consequential.

Conclusions

The bromination of veratrole in acetic acid occurs by a conventional electrophilic aromatic substitution mechanism involving a late rate-limiting and product-determining transition state for formation of the σ-complex. However, the Friedel-Crafts acylations of veratrole, using $AgClO_4$ or $AlBr_3$, are not so simple. The intermolecular and intramolecular ^{13}C KIEs do not fit with each other, establishing that the rate-limiting and product-determining steps have separated.

The small but significant intermolecular KIE obtained for the acylation of veratrole using $AgClO_4$ is consistent with a rate-limiting carbon-carbon bond formation. Which is expected for this kind of reaction. However, the unity intramolecular KIE suggests that the reaction is affected by a bifurcating energy surface. As described above, an early transition state followed by a bifurcating energy surface will decreased the observed intramolecular KIE, in this case we cannot see a significant KIE.

In the case of the acylation of veratrole using $AlBr_3$, the negligible intermolecular KIE could be consistent with either rate-limiting diffusion or a very early transition state for electrophilic attack, and reactivity studies favor the latter. The more extraordinary inverse intramolecular ^{13}C KIE cannot be reconciled with any ordinary over-the-barrier step. From analogy with other systems proposed to involve bifurcating energy surfaces,

we would suggest that the inverse KIE is characteristic of the involvement of dynamics on bifurcating energy surfaces.

Even though the nature of the rate-limiting step for the different acylation conditions is not the same, there is enough evidence to support the involvement of a bifurcating energy surface in the product-determining step of both of these reactions. This experimentally-based conclusion is supported by computational studies. The approach of an acetylium ion to veratrole is computationally predicted to involve an enthalpically barrierless bifurcating energy surface. Electrostatic effects and frontier orbital interactions favor an initially symmetrical approach of the electrophile, with desymmetrization eventually occurring after the variational transition state due to the greater stability of the unsymmetrical σ-complexes. The energy surface for approach of the electrophile would necessarily be made unsymmetrical by the presence of solvent and the counterion. Trajectory studies suggest that the solvent asymmetry does not fully control the product, allowing the selectivity seen in the inverse ^{13}C KIE to occur. However, a tightly-bound counterion as in **16**‡ would preordain the product, and this indicates that the counterion is not tightly associated at the transition state.

The observations for the acylation of veratrole suggest a more general reinterpretation of selectivity observations in electrophilic aromatic substitutions. Because bifurcating energy surfaces can lead to selectivity that reflects the product stability, success in the Brown selectivity relationship can be the result of two kinetically-distinguishable steps with no intermediate. Selectivity under any circumstances requires that trajectories be partitioned along separate pathways, but that

partitioning may occur either before or after the rate-limiting transition state. The two possibilities exist along a continuum, uniting the understanding of selectivity in electrophilic aromatic substitutions.

Experimental and Computational Procedures

Acylation of veratrole using $AgClO_4$ for intramolecular KIEs example procedure. A mixture of 5.00 g (36.19 mmol) of veratrole, 15.00 g (72.37 mmol) of silver perchlorate and 7.96 mL (36.19 mmol) of 2,6-di-tert-butylpyridine in 20.11 mL of CH_2Cl_2 was cooled to 0 °C. To this mixture were added, dropwise, 3.86 mL (54.28 mmol) of acetyl chloride. After an additional of 22 hours of stirring, the reaction was quenched by the addition of 15 mL of water. The reaction mixture was extracted with 15 mL of ether (3 times) and the organic layer was dried over sodium sulfate. The volatiles were removed on a rotary evaporator and the residue was chromatographed on silica gel using 20% EtOAc/hexanes as eluent to aford 1.12 g of 3,4-dimethoxyacetophenone (**6**). ^{1}H NMR ($CDCl_3$) δ 7.93 (m, 2 H), 6.93 (m, 2 H), 3.86 (s, 3 H), 2.55 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 197.0, 153.5, 149.2, 130.7, 123.5, 110.2, 110.1, 56.1, 26.4.

Acylation of veratrole using $AlBr_3$ for intramolecular KIEs example procedure. A solution of 2.93 g (11 mmol) of $AlBr_3$ in 5 mL of CH_2Cl_2 was added to a mixture of 3.10 g (22 mmol) of veratrole and 0.78 mL (11 mol) of acetyl chloride in 220 mL of CH_2Cl_2 while stirring under N_2 at 25 °C. The conversion was 46% after 4 h based on NMR analysis of aliquots. The reaction mixture was washed successively with 100 mL of 1 M HCl and 100 mL of water, then dried over $MgSO_4$. The volatiles were removed

on a rotary evaporator, and the residue oil was chromatographed on a 65 mm x 300 mm flash silica gel column using CH_2Cl_2 as eluent, followed by a second chromatography on a 33 mm x 300 mm flash silica gel column using 20% EtOAc/hexanes as eluent. The resulting crude product was recrystallized from petroleum ether to afford 398 mg of **6**.

Closely analogous reactions in CH_2Cl_2 and in 1,2-dichlorobenzene were carried out to obtain a total of four independent samples of **6** for NMR analysis.

Acylation of veratrole using $AgClO_4$ for intermolecular KIEs example procedure. A mixture of 5.00 g (36.19 mmol) of veratrole and 15.00 g (72.37 mmol) of silver perchlorate and 7.96 mL (36.19 mmol) of 2,6-di-tert-butylpyridine in 20.11 mL of CH_2Cl_2 was cooled to 0°C, and 3.86 mL (54.28 mmol) of acetyl chloride were added dropwise. After an additional of 24 hours of stirring, the reaction was quenched by the addition of 15 mL of water. The reaction mixture was extracted with 15 mL of ether (3 times) and the organic layer was dried over sodium sulfate. The volatiles were removed on a rotary evaporator and the residue was chromatographed on a silica gel using 20% EtOAc/hexanes as eluent and 0.22 g of veratrole (**5**) was reisolated.

Acylation of veratrole using $AlBr_3$ for intermolecular KIEs example procedure. A solution of 41.81 g (157 mmol) of $AlBr_3$ in 75 mL of CH_2Cl_2 was added to a mixture of 20.726 g (150 mmol) of veratrole (**5**) and 13 mL (183 mmol) of acetyl chloride in 1.5 L of CH_2Cl_2 while stirring under N_2 at 25 °C. After 6 h the conversion was 82% based on NMR analysis of an aliquot. The reaction mixture was washed successively with 1 M HCl and water, then dried over $MgSO_4$, and the volatiles were removed on a rotary evaporator. The residue was chromatographed successively on three flash silica gel

columns using 20% EtOAc/hexanes as eluent to afford 0.60 g of the unreacted **5**. An analogous reaction using 20.731 g of **5** was taken to 86% conversion and 1.10 g of **5** was reisolated.

Preparation of veratrole-d_4. A mixture of 15 g (0.11 mol) of veratrole in 100 mL of D_2O and 15 mL of H_2SO_4 was refluxed for 8 d, at which time NMR analysis of an aliquot indicated a deuterium incorporation of 83%. The reaction mixture was cooled and the layers were allowed to separate overnight. The veratrole layer was then refluxed for 14 with 100 mL of D_2O and 15 mL of D_2SO_4 for 14 d. The mixture was cooled and extracted with 20 mL of CH_2Cl_2. The organic layer was rinsed with two 10-mL portions of D_2O, dried (Na_2SO_4), and distilled to afford 10 g (65%) of veratrole-d_4 with 98.7% deuterium incorporation by ^1H NMR analysis. Veratrole-d_4: ^{1}HNMR (C_6D_6) δ6.78(m, 0.28 H), 6.60 (m, 0.29 H), 3.37 (s, 6 H). The CI-MS m/e 142:141 ($C_8H_6D_4O_2^+$ / $C_8H_7D_3O_2^+$) ion intensity ratio was 65.5:34.5.

Acylation of veratrole / veratrole-d_4 using $AlBr_3$ for H/D KIEs example procedure. To a mixture of 0.345 g (2.5 mmol) of veratrole and 0.355 g (2.5 mmol) of veratrole-d_4 in 50 mL of CH_2Cl_2 was added 0.36 mL (5 mmol) of acetyl chloride followed by 1.355 g (5 mmol) of $AlBr_3$ in 2.5 mL of CH_2Cl_2. The reaction was allowed to stir for 3 min, then quenched by the addition of 200 mL of saturated $NaHCO_3$ solution. The mixture was extracted with 200 mL of CH_2Cl_2, and the organic layer was washed with water and dried over Na_2SO_4. The volatiles were removed on a rotary evaporator. GC analysis of the residue indicated approximately 6% conversion. The

residue was chromatographed on silica gel CH_2Cl_2 as eluent to afford 35 mg of **6** / **6**-d_3 in a ratio of 1.01 : 1 by NMR analysis.

Bromination of veratrole for intramolecular KIEs example procedure. A mixture of 8 g (50 mmol) of Br_2 in 30 mL of acetic acid was added dropwise over 1 h to a stirred solution of 6.901 g (0.05 mol) of veratrole in 20 mL of acetic acid at 0 °C. The reaction was monitored by NMR analysis of aliquots, and after 1 h the conversion was 93%. The bulk of the acetic acid was then removed by vacuum distillation, and the resultant oil was taken up in 25 mL of petroleum ether and washed successively with 5% sodium hydroxide and water, then dried over Na_2SO_4. The volatiles were removed on a rotary evaporator and the residue was distilled under vacuum to afford 2.9 g (27%) of 4-bromoveratrole (**7**). An analogous reaction using 6.905 g of veratrole was taken to 95% conversion and 2.0 g of **7** was isolated. ^{1}H NMR ($CDCl_3$) δ 6.72-6.76 (m, 2 H), 6.71 (d *J*=8.4 Hz, 1 H), 3.83 (s, 3 H), 3.81 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 149.8, 148.4, 123.4, 114.8, 112.7, 112.6, 56.1, 56.0

Bromination of veratrole for intermolecular KIEs example procedure. A mixture of 19 g (120 mmol) of Br_2 in 72 mL of acetic acid was added dropwise over 2 h to a stirred solution of 20.727 g (0.15 mol) of veratrole in 60 mL of acetic acid at 0 °C. The reaction was monitored by NMR analysis of aliquots, and after 2 h the conversion was 77%. The bulk of the acetic acid was then removed by vacuum distillation, and the resultant oil was taken up in 50 mL of petroleum ether and washed successively with 5% sodium hydroxide and water, then dried over Na_2SO_4. The volatiles were removed on a rotary evaporator and the residue was fractionally distilled under vacuum to afford 1.2 g

(6%) of the unreacted **5**. An analogous reaction using 20.730 g of veratrole was taken to 74% conversion.

Acylation of butyl phenyl ether using $AlCl_3$ for intermolecular KIEs example procedure. A mixture of 8.32 g (55 mmol) of butyl phenyl ether (**8**) and 5.2 g (39 mmol) of anhydrous aluminum chloride in 30 mL of CH_2Cl_2 was cooled to 0 °C, and 4.86 g (62 mmol) of acetyl chloride was added dropwise over 3 min. After an additional 10 s of stirring, the reaction was quenched by the addition of 50 mL of water. The reaction mixture was extracted with 50 mL of ether and the organic layer was dried over sodium sulfate. The volatiles were removed on a rotary evaporator, and the conversion was determined to be 65% by NMR analysis. The residue was chromatographed on a 5 cm x 20 cm silica gel column chromatography using hexanes as eluent to afford 2.66 g of the unreacted **8**. An analogous reaction using 8.32 g was taken to 75% conversion and 0.62 g of **8** was isolated.

Procedure for NMR measurements. Samples were prepared in 5-mm NMR tubes filled with $CDCl_3$ or C_6D_6 to a constant height of 5.0 cm, and the intermolecular KIE measurements involving a comparison of sample versus standard used a constant amount of analyte (250 or 400 mg for samples of recovered veratrole from acylation, using $AgClO_4$ and $AlBr_3$ respectively; and 650 mg for samples of recovered veratrole from bromination). The ^{13}C NMR spectra were recorded at 125.701 MHz with inverse gated decoupling. A T1 measurement was performed on each sample to ensure that the relaxation rates did not change from sample to sample. Integrations were determined numerically using a constant integration region for each peak based on peak width. The

^{13}C spectra of **6** were taken using 86.5-s delays between calibrated 90° pulses, 9.000-s acquisition time, and collecting 503,872 points. For comparison of each relevant pair of peaks, a set of spectra was taken with the transmitter centered between the two peaks. The ^{13}C spectra of veratrole were taken using 72-s delays between calibrated 90° pulses, a 14.221-s acquisition time, and collecting 512,000 points. The ^{1}H spectra of **6** / **6**-d_3 were taken using 10-s delays between calibrated 90° pulses, a 3.744-s acquisition time, and collecting 41932 points. The ^{13}C spectra of **7** were taken using 69-s delays between calibrated 90° pulses, a 10.669-s acquisition time, and collecting 512000 points. The ^{13}C spectra of **8** were taken using 30-s delays between calibrated 90° pulses, an 8.6-s acquisition time, and collecting 524288 points. The resulting ^{13}C integrations for the spectra are provided in the Appendix, along with sample spectra, and the KIEs were calculated as previously described.

General computational procedures. Standard calculations of minima or transition structures employed either Gaussian 03 or Gaussian 09. Default procedures were employed unless otherwise noted. The use of Gaussian 03 versus Gaussian 09 only makes a difference here in the PCM calculations. By default, Gaussian 09 PCM calculations used UFF radii, while the Gaussian 03 PCM calculations used UA0 radii. Although there are some advantages to the Gaussian 09 procedures, the B3LYP PCM calculations had already been carried out in Gaussian 03. Spot checks using Gaussian 09 B3LYP/PCM calculations did not exhibit any qualitative differences (see a later section). Of course, care was taken not to mix Gaussian 03 and Gaussian 09 results for any energy calculation. All M06-2X calculations employed Gaussian 09. PCM calculations used

dichloromethane as the solvent unless otherwise noted. To model acetic acid in Gaussian 03 calculations, the parameters eps, rsolv, and density were set at 6.20, 2.21, and 0.0105, respectively. All absolute energies are in Hartrees. All relative energies are presented in kcal/mol. Full structures and energetics are provided in a section below.

The program suite PROGDYN used for dynamics is a series of component programs written as either Unix shell scripts or awk programs. Gaussian09 was used to calculate the forces at each point in trajectories. A full description of PROGDYN and the parameters employed can be found in a later section. The newest version of this program can be obtained from Daniel Singleton of Texas A&M.

Approximate canonical variational transition structures for the attack of an acylium ion on veratrole were located in one of two ways. The first way involved fixing the distance between the acylium carbon and the C4 and C5 carbons of veratrole at a series of equal values and obtaining a series of relaxed structures. For each structure, frequency calculations were carried out and free energies were calculated using the harmonic approximation without scaling. The structure reported was the free energy maximum along this path. The second procedure was adapted from the "nosaddle" procedure in the program POLYRATE, used first by Truhlar for the reaction of O with OH. The starting point fixed the two carbon-carbon distances at 4.0 Å, optimizing all other coordinates. From this structure, a steepest-descent path in mass-weighted coordinates was followed as described in the Supporting Information for a previous publication in this laboratory. At regular intervals along the steepest-descent path, frequency calculations were carried out and free energies were calculated using the

harmonic approximation without scaling. The structure reported was the free energy maximum along this path.

Initialization of trajectories. For Model 66, an initial structure placing **14**‡ in the center of 66 CH_2Cl_2 molecules was generated by hand. The C4, C5, and Cα carbons were constrained in position with Cα-C4 = Cα-C5 = 3.1 Å, and the CH_2Cl_2 molecules were constricted to a 19.8 Å cubic box using a classical-trajectory equilibration in PM3 calculations at 2000 K for 3 ps and employing the "box" facility in PROGDYN. (The constriction of the atoms into the box works by an algorithm that reverses the momentum of atoms moving away from the boundary of the box.) The trajectory was then cooled slowly to 298.15 using the thermostat facility in PROGDYN with thermostatmult set at 0.999 (removing 0.1% of the energy per fs), and equilibration at 298.15 K was continued for 10 ps. The method for force calculation was then switched to ONIOM using M06-2X/6-31G* for all of the atoms of **14**‡ and using PM3 for the CH_2Cl_2 molecules, and the trajectory was continued for 1 ps. The trajectory was continued for 9 ps, and at 250 fs intervals the helper program *progdynsam* (described in a later section) was used to create a *geoPlusVel* file for use in PROGDYN. The *progdynsam* program continues all atoms along their current trajectories, with the exception of atoms that were fixed in position. For the latter atoms, *progdynsam* gives them independent Boltzmann-random velocities based on the temperature. The resulting unconstrained trajectories were integrated forward and backward in time using direct dynamics until either **12** or **12'** were formed.

The trajectories looking at the product distribution from **16**‡ were quasiclassical,

i. e. including zero-point energy plus a Boltzmann distribution of quantized vibrational energies for each mode. The trajectories looking at ion pairing in **16**‡ were carried out in fully classical mode, i. e. including only a classical Boltzmann distribution of energy. For the quasiclassical trajectories, the desired energy in each of the normal modes was mapped from a random number generator to a Boltzmann distribution set at 25 °C. The phase of each of the normal modes was mapped from a Gaussian distribution of random numbers. This distribution is not correct for a classical oscillator but would be approximately correct for a quantum oscillator in its ground state (only ignoring mode displacements outside of the classical limit), and has the advantage that a larger portion of the trajectories start with an energy approximating the initially desired energy. The sign on the velocity of the normal modes was randomized. After an energy/force calculation on the initial geometry, the total initial energy was calculated and the trajectory was thrown out if the energy did not agree satisfactorily (within 1 kcal/mol) with the desired energy. (This is a variation of the conventional practice of scaling energies.) The mode corresponding to the transition vector was treated classically. For the classical trajectories, the displacements along the normal modes were turned off, and the modes were given a randomized Boltzmann distribution of energy.

Simulated annealing for Model 22 was carried out by initiating classical trajectories at 600 K and cycling down to 0 K and back up to 600 K using the thermostat facility in PROGDYN with thermostatmult set at 0.998 to lower the temperature and 1.01 to raise the temperature. The low-temperature structures were then extracted and optimized in an ordinary geometry optimization. A total of twelve structures were

optimized in this way, and the best of these was **15**.

KIE predictions. For the various transition structures versus the appropriate lowest-energy conformation of either **5** or benzene, conventional TST isotope effects were calculated by the method of Bigeleisen and Mayer using the program QUIVER, modified for easier use with Gaussian 09 and compilation on modern compilers. The conventional TST isotope effects were then corrected by a one-dimensional infinite-parabola tunneling correction. The modified QUIVER program, macros that aid in running the program, and a spreadsheet that carries out the isotope effect calculations is available on request, and we have supplied this material to over 20 groups. For simplicity, we have adopted the practice of using a single frequency scaling factor of 0.9614 in all cases. Within a reasonable range, the choice of scaling factor has a negligible effect on the predicted value of any small ^{13}C KIE and it affects large ^{13}C KIEs by no more than 0.002. We note that the applicability of any particular literature scaling factor to carbon isotope effects is questionable.

CHAPTER IV

THE MECHANISM OF INTERMOLECULAR COPE-TYPE HYDROAMINATION OF ALKYNES

Introduction

Hydroaminations of alkenes and alkynes is one of the simplest and most desired synthetic transformations. However, no general method to achieve this has been developed. This transformation consists of the direct formation of a new C – N bond by addition of an amine to an unsaturated C – C bond.[146] For many years, researchers have focused their attention into the development of new methods to accomplish this transformation in order to access the synthesis of nitrogen containing molecules. Acid and base catalyzed reactions have been generally used for this purpose.[146-147] In addition, transition metal catalysis[146-148] has been used in order to activate unsaturated C – C bonds and subsequently add a nitrogen-containing moiety. Nonetheless, the reactions that are tolerated by these methodologies are very limited and have low regioselectivity. For the metal catalyzed reactions, high sensitivity to air and moisture has been observed.[147] In order to overcome these limitations, many researchers continue to explore this area.

In 1976, House and co-workers made an interesting discovery; they observed that a classical reaction, known as the Cope elimination, seemed to have gone backwards. In the reaction shown in Figure 4 – 1, the formation of the pyrrolidine suggested that the

oxyme did an intramolecular addition to one of the alkenes, this reaction was referred to as a Cope-type hydroamination.[149]

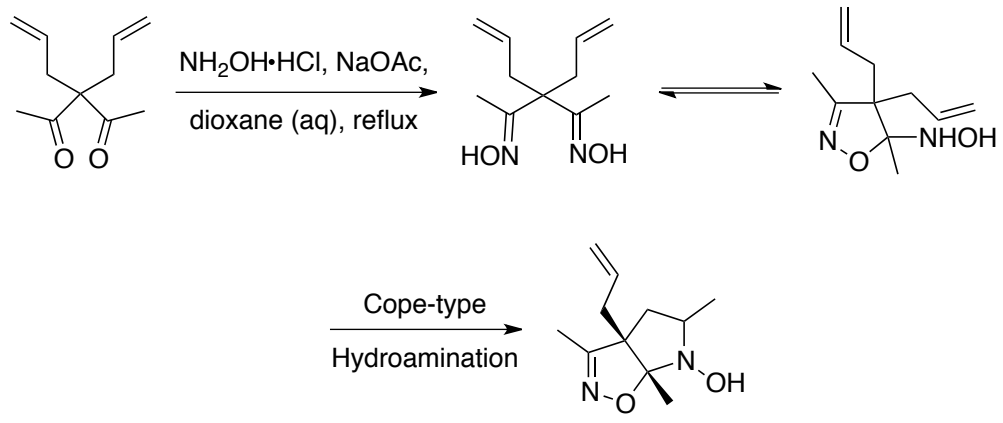


Figure 4 - 1: First reported Cope-type hydroamination

A Cope elimination reaction consists of the *syn* elimination of tertiary amine oxides to afford an alkene and a hydroxylamine. The mechanism for this transformation has been well studied and is known to proceed via a concerted pathway with a cyclic 5-membered transition state (Figure 4 – 2).[150-151] This new observation (the addition of the oxyme to the alkene) caught the attention of many scientists who have studied the substrate scope, solvent and substituent effects, and also the mechanism for this reaction.[147, 149-150, 152-154] The first proposed mechanism for this transformation, presented by House, suggested that it proceeded via a radical pathway. Later, in the early 90's, another mechanistic proposal suggested that the reaction proceeded via a concerted,

synchronous mechanism with a 5-membered ring TS, similar to the one involved in the cope elimination reaction (Figure 4 – 2).[149] This mechanism was based on results reported by Black, Doyle, Ciganek and Oppolzer.

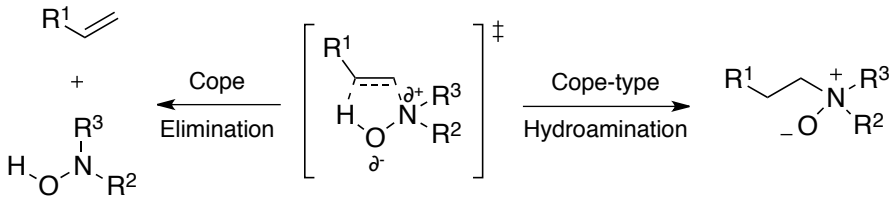


Figure 4 - 2: Transition state for Cope elimination and Cope-type hydroamination

After this discovery, a significant amount of studies have been done in order to understand the behavior of this transformation and develop applications for this technique. Holmes and Houk, have carried out a series of competition experiments, and computational studies in order to understand how substitution, tether length, stability, and strain of the substrates can affect the products and the rate of the cyclization process.[152] In this work, they demonstrated that the reactivity and major product of an intramolecular Cope-type hydroamination could be affected by: the tether length and the substituents present on the distal carbon of the alkenes. Computational studies demonstrated that the conformation of the tether length at the TS is the factor that determinates the major product for this transformation. Also, it showed that the reaction proceeds via a concerted 5-membered, planar TS, rather than a radical pathway.

Up to this point, this reaction was mostly used for *intra*molecular processes. However, the increased interest in finding applications for this new approach lead Beauchemin and co-workers to develop a methodology that allowed them to perform *inter*molecular Cope-type hydroaminations.[147-148] Recently, an extensive experimental and computational study by Beauchemin[148] demonstrated that this transformation could also be used for intermolecular hydroaminations of alkenes and alkynes. In this work, they found that the reactivity of akynes was higher than that of alkenes. In addition, the experimental results showed that the reactivity of the unsaturated compounds was highly dependent of their stability, and that solvents also affected the rate and yield of these reactions. Computational results showed that the polarity of the solvent has a huge impact in the rate of the reaction and that the proton transfer step was, in fact, the rate limiting step for the hydroamination process.

In order to have a better understanding of the selectivity and mechanistic pathway of this reaction we decided to study the Cope-type hydroamination of phenylacetylene and *p*-chloro-phenylacetylene. Our study combines experimentally determined ^{13}C KIEs at natural abundance and computational studies, used to explain the experimental results.

Results and Discussion

The hydroamination of phenylacetylene (**1a**) and *p*-chlorophenylacetylene (**1b**) were chosen for this study. These two substrates showed a very high selectivity for the functionalization at the internal carbon of the alkyne (Figure 4 – 3), this was desirable

because a mixture of products will complicate the observed experimental isotope effects. The reaction of **1a** with hydroxylamine afforded ~5% of the minor isomer **3a**, while the reaction of **1b** under the same conditions formed ~7% of the minor isomer **3b**, as determined by ^{1}H NMR. These small percentages of the minor product will not affect the KIEs observed for the functionalized positions.

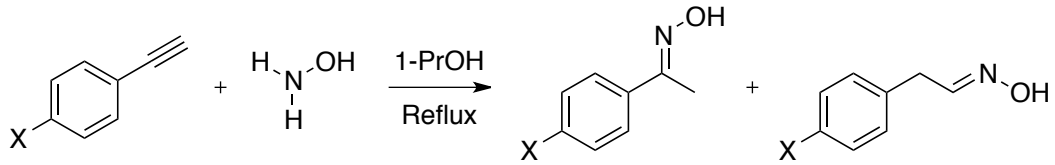


Figure 4 - 3: Cope-type hydroamination reactions under study

Experimental intermolecular KIEs. The intermolecular ^{13}C KIEs for the Cope-type hydroamination of phenylacetylene were determined combinatorialy at natural abundance by NMR methodology. Hydroaminations of **1a** were taken to 70% ± 2% convertion, determined by ^{1}H NMR. The unreacted **1a** was recoverd from the reaction mixture by an aqueous workup followed by column chromatography. The samples were analyzed by ^{13}C NMR, and the isotopic composition was compared to standards prepared from starting material that had not been submitted to the reaction conditions. KIEs were then calculated based on the isotopic composition ratio of sample vs standard,

using the Singleton method.[34] A similar process was employed for the preparation of the samples of **1b**. The calculated KIEs are shown in Figure 4 – 4.

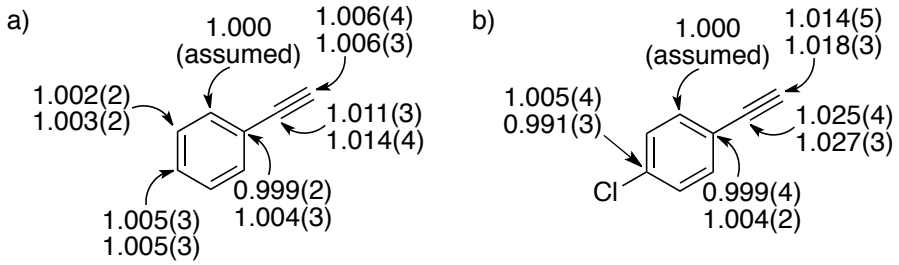


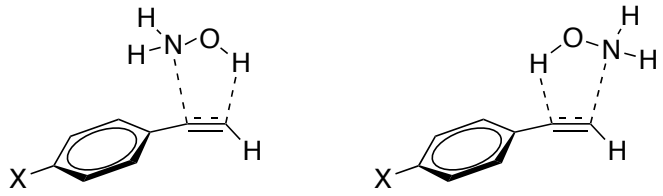
Figure 4 - 4: Experimentally observed intermolecular kinetic isotope effects for the Cope-type hydroamination

An interesting observation, when we compared the KIEs for the different alkynes, is that the isotope effects for phenylacetylene are significantly smaller that the ones obtained for the *p*-chloro-phenylacetylene. We believe that the smaller isotope effect is due to the evaporation of the phenylacetylene while the reaction was running. All the necessary precautions to avoid this complication were followed, however this is still a possibility. The evaporation of the starting material could potentially decrease the observed KIE. Even though the isotope effects are different for each alkyne, we can still qualitatively compare the results.

An important qualitative observation is that, for both compounds, the internal carbon shows a bigger isotope effect. This KIE corresponds to the C – N bond formation

at the TS. This is expected, since carbon and nitrogen are both heavy atoms forming a bond at the rate-limiting step.

Computational calculations for KIE predictions. In order to understand the mechanism involved in this reaction we sought to locate the TSs and intermediates involved in the process. This was done using Gaussian09; the TSs and intermediates were located using multiple methods and basis sets. In general, all the calculations showed that the Cope-type hydroamination proceeds via an asynchronous concerted TS (Figure 4 – 5).



4a X=H, 28.6 kcal/mol
4b X=Cl, 29.1 kcal/mol

5a X=H, 31.7 kcal/mol
5b X=Cl, 31.8 kcal/mol

Figure 4 - 5: Transition states and free energies for the products of the hydroamination of **1a** and **1b**

Using the TSs calculated for the major product of the reaction we sought to predict the experimental KIEs using QUIVER. The results are summarized in Tables 4 – 1 and 4 – 2. In addition, the tables include the C – N and the C – H bond distances.

Table 4 - 1: Predicted KIEs and the bond distances for the C – H and C – N at the TSs for phenylacetylene (**1a**)

Method/Basis Set	**KIEs***		**Distance**	
	Internal C	*Terminal C*	*C – H*	*C – N*
M06-2X/6-31+G**	1.026	1.012	1.947	1.584
M06/6-31+G**	1.029	1.009	1.494	1.987
B1B95/6-31+G**	1.029	1.009	1.507	2.001
PBEh1PBE/6-31+G**	1.022	1.012	1.495	2.046
B972/6-31+G**	1.018	1.011	1.456	2.063
B3P86/6-31+G**	1.029	1.012	1.471	2.073
B3PW91/6-31+G**	1.019	1.011	1.461	2.078
B3LYP/6-31+G**	1.016	1.008	1.419	2.087
B3LYP/6-31+G** (PCM)	1.017	1.011	1.415	2.106

Table 4 - 2: Predicted KIEs and the bond distances for the C – H and C – N at the TSs for *p*-chloro phenylacetylene (**1b**)

Method/Basis Set	**KIEs***		**Distance**	
	Internal C	*Terminal C*	*C – H*	*C – N*
M06-2X/6-31+G**	1.025	1.012	1.585	1.943
M06/6-31+G**	1.028	1.009	1.502	1.983
B1B95/6-31+G**	1.024	1.013	1.507	1.996
PBEh1PBE/6-31+G**	1.022	1.012	1.499	2.040
B972/6-31+G**	1.019	1.011	1.454	2.061
B3P86/6-31+G**	1.016	1.008	1.417	2.086
B3PW91/6-31+G**	1.019	1.011	1.459	2.077
B3LYP/6-31+G**	1.016	1.008	1.417	2.087
B3LYP/6-31+G** (PCM)	1.017	1.012	1.459	2.099

When comparing the predicted KIEs with the obtained experimentally, we found that Transition State Theory explains very well the mechanism for this reaction. However, the same method does not explain the experimental KIEs for both reactions. In the case of **1a**, we found that the method that best predicts the results best is B3LYP/6-31+G** in gas phase. For alkyne **1b**, we found that the method that best explains the

experimental results was M06-2X/6-31+G**, also in gas phase. With these results in hand we concluded that the reaction proceeds via the reverse mechanism of the Cope elimination reaction. Which involves a rate limiting cyclic, asynchronous, 5-membered ring TS, as proposed in the literature.[146, 148, 155]

An interesting observation from these predicted KIEs is the small tendency that the bond distances vs the KIE have. In the C – N bond case, we can see that as the distance gets bigger, the KIEs get smaller. However, the opposite is observed for the C – H bond. Determination of KIEs has long been used to get insight into the structure of the rate-limiting TS that will eventually lead to the product of a determined reaction. The results obtain from the predicted KIEs are very important, because they reflect how the TS structure will affect the observed KIEs.

Conclusions

In this chapter we studied the Cope-type hydroamination of phenylacetylene (**1a**) and *p*-chloro phenylacetylene (**1b**) using hydroxylamine. The reaction was studied employing a combination of experimentally determined KIEs and computational calculations. The computational calculations and KIE predictions showed that TST can effectively explain the experimental results. As proposed in literature, the reaction proceeds via a 5-member TS that resembles the one involved in the Cope elimination reaction.

In addition, the predicted KIEs from multiple calculated TSs showed a correlation between bond distance and observed KIE. These results show the importance

of KIEs when studying a reaction's mechanism. As mention before, the determination of KIEs has always been considered the most accurate method for understanding the structure of TSs in mechanistic studies. Our results, once again, show the importance of KIE determinations when trying to understand a particular mechanistic pathway.

Experimental and Computational Procedures

Hydroamination of phenylacetylene. A mixture of 63.70 mL of 1-propanol (2 M), phenylacetylene **1a** (13.00 g, 127.46 mmol) and hydroxylamine solution (50 % hydroxylamine in water, 21.05 g, 318.63 mmol) was reflux at ~ 90 ºC. The reaction's progress was followed using ^{1}H NMR, until 70 % conversion. Reaction was stopped by addition of a saturated $NaHCO_3$ solution and the mixture was extracted with pentanes. Combined extracts were washed several times with water, dried over Na_2SO_4 and concentrated in vacuum. Starting material was recovered from crude mixture by column chromatography using pentanes.

Synthesis of 1-chloro-4-(1,1,2,2-tetrabromoethyl)benzene. Bromide was added dropwise to a solution of 4-chlorostyrene (14.00 g, 100.3 mmols) in 100 mL of CH_2Cl_2 (1M) until the brown/orange color persisted. The mixture was then concentrated under vacumm. The residual solid was purified via column chromatography using Silica gel and Hexanes as the eluent to yield 22.00 g (98% yield) of a mixture of enantiomers. The product was obtained as a white solid.

Synthesis of p-chlorophenylacetylene. Potassium tert-butoxide (23.64 g, 210.42 mmol) was added in small portions to a solution of 21.00 g of 1-chloro-4-(1,1,2,2-

tetrabromoethyl)benzene (70.14 mmols) in 140 mL of THF (0.5 M). After the addition, the reaction mixture was left stirring for 24 h under reflux, with a N_2 atmosphere. The reaction was quenched by addition of 50 mL of water. The layers were separated, and the water layer was extracted with diethyl ether. Combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residual solid was purified via column chromatography using Silica gel and hexanes as the eluent to yield 5.02 g (52% yield) of the *p*-chlorophenylacetylene as a white solid.

Hydroamination of p-chlorophenylacetylene. A mixture of 32.7 mL of 1-propanol (1 M), *p*-chlorophenylacetylene **1b** (4.50 g, 32.71 mmol) and hydroxylamine solution (50 % hydroxylamine in water, 5.01 mL, 81.78 mmol) was reflux at ~ 90 ºC. The reaction's progress was followed using ^{1}H NMR, until 70 % conversion. Reaction was stopped by addition of a saturated $NaHCO_3$ solution and the mixture was extracted with pentanes. Combined extracts were washed several times with water, dried over Na_2SO_4 and concentrated in vacuum. Starting material was recovered from crude mixture by column chromatography using hexanes.

KIE determination for phenylacetylene NMR samples. All NMR samples consisted of approximately 300 mg of the phenylacetylene in 5 mm NMR tubes filled to a constant height of 5 cm with d_6-benzene. The ^{13}C spectra were recorded at 125.51 MHz using inverse gated decoupling, 138.5 s delays between calibrated $\pi/2$ pulses, and 12 s acquisition time. The 138.5 s delay was based on the T1 of the signal at 83.67 ppm, which was measured to be 23.1 s. Integrations were numerically determined using a constant integration region for each peak. A zero-order baseline correction was generally

applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction was ever applied. A total number of 6 spectra were recorded for each sample and standard. The integration value of each peak was determined by the average of all measurements. The uncertainty of the measurements was determined by considering a two-side 95 % confidence interval in a T-distribution.

KIE determination for p-chlorophenylacetylene NMR samples. All NMR samples consisted of approximately 250 mg of the *p*-chloro phenylacetylene in 5 mm NMR tubes filled to a constant height of 5 cm with d_6-DMSO. The ^{13}C spectra were recorded at 125.51 MHz using inverse gated decoupling, 138.5 s delays between calibrated $\pi/2$ pulses, and 5 s acquisition time. The 147.2 s delay was based on the T1 of the signal at 82.7 ppm, which was measured to be 24.53 s. Integrations were numerically determined using a constant integration region for each peak. A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction was ever applied. A total number of 6 spectra were recorded for each sample and standard. The integration value of each peak was determined by the average of all measurements. The uncertainty of the measurements was determined by considering a two-side 95 % confidence interval in a T-distribution.

General computational procedure. Calculations of structures, energies, and frequencies employed default procedures in Gaussian09 unless otherwise noted. Complete structures and energetics are provided in Appendix B. All absolute energies are in Hartrees. All relative energies are presented in kcal/mol.

KIE predictions. For the various transition structures calculated for the major product, **2a** or **2b**, versus the appropriate lowest-energy conformation of **1a** or **1b**, conventional TST isotope effects were calculated by the method of Bigeleisen and Mayer using the program QUIVER, modified for easier use with Gaussian 09 and compilation on modern compilers. The conventional TST isotope effects were then corrected by a one-dimensional infinite-parabola tunneling correction. For simplicity, we have adopted the practice of using a single frequency scaling factor of 0.9614 in all cases. Within a reasonable range, the choice of scaling factor has a negligible effect on the predicted value of any small ^{13}C KIE and it affects large ^{13}C KIEs by no more than 0.002. We note that the applicability of any particular literature scaling factor to carbon isotope effects is questionable.

CHAPTER V

DIELS-ALDER REACTIONS: EXPLORING THE POSSIBILITY OF HIDDEN TRANSITION STATES AND ENTROPIC INTERMEDIATES

Introduction

Cycloadditions, in general, are considered very important reactions in organic chemistry. This is mainly because these transformations can incorporate multiple stereocenters via a single synthetic step, with minimum waste. In particular, Diels-Alder cycloaddition reactions are considered one of the most important transformations in organic chemistry, due to the complexity of the products that can be achieved. The reaction consists of the formation of two new C – C σ-bonds while incorporating up to four new stereocenters on the product.[156-157] Historically, it was thought that the reaction proceeded via a concerted and synchronous TS. However, previous studies have shown that this reaction can proceed via asynchronous TS, and that this is mostly affected by the substituents in the dienophile or the diene used.[158]

Physical organic chemistry has always focus on the mechanistic understanding of reactions. A mechanism is typically described by using TST, however this approach has not always been able to explain experimental observations. When TST fails to explain experimental observations, physical organic chemists suggest the possibility of dynamic effects been involved in the reactions. Based on literature results, it has been suggested that dynamic effects could potentially affect Diels-Alder cycloadditions. In particular, it

has been proposed that non-statistical recrossing could be involved in certain types of Diels-Alder reactions.[19, 27, 159] This dynamic effect refers to the trajectories that after passing the TS they return to starting materials (Figure 5 – 1).

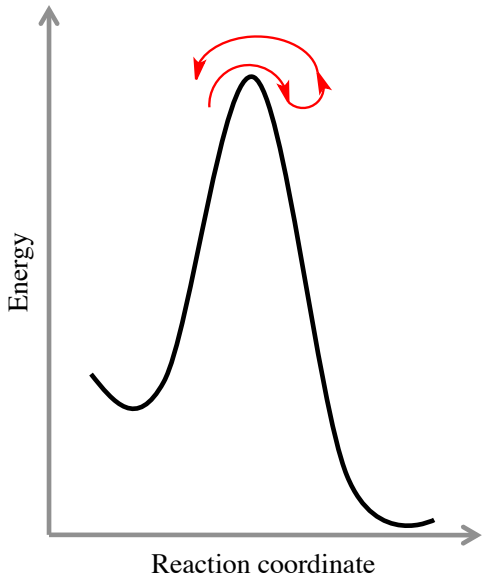


Figure 5 - 1: Representation of recrossing as a dynamic effect

Even though it is known that some recrossing can happen, it has been proven that in some systems the extent of recrossing depends on the nature of the system, and it can affect the selectivity of the process. Intrigued by some preliminary results, our group decided to look for systems that could be affected by non-statistical recrossing. The preliminary computational results suggested that the product ratio for the Diels-Alder cycloaddition between the vinylium ion of *trans*-cinnamaldehyde and cyclopentadiene

(Figure 5 – 2 (a)) arise from non-statistical recrossing caused by the existence of an entropic intermediate.[19] This intermediate cannot be predicted using TST, because the potential energy surface will only show a single saddle point giving the appearance of a simple concerted cycloaddition. However, when VTST is used, the free energy surface showed the presence of an intermediate for which a second, and rate-limiting step will lead to the desired product (Figure 5 – 2 (b)).

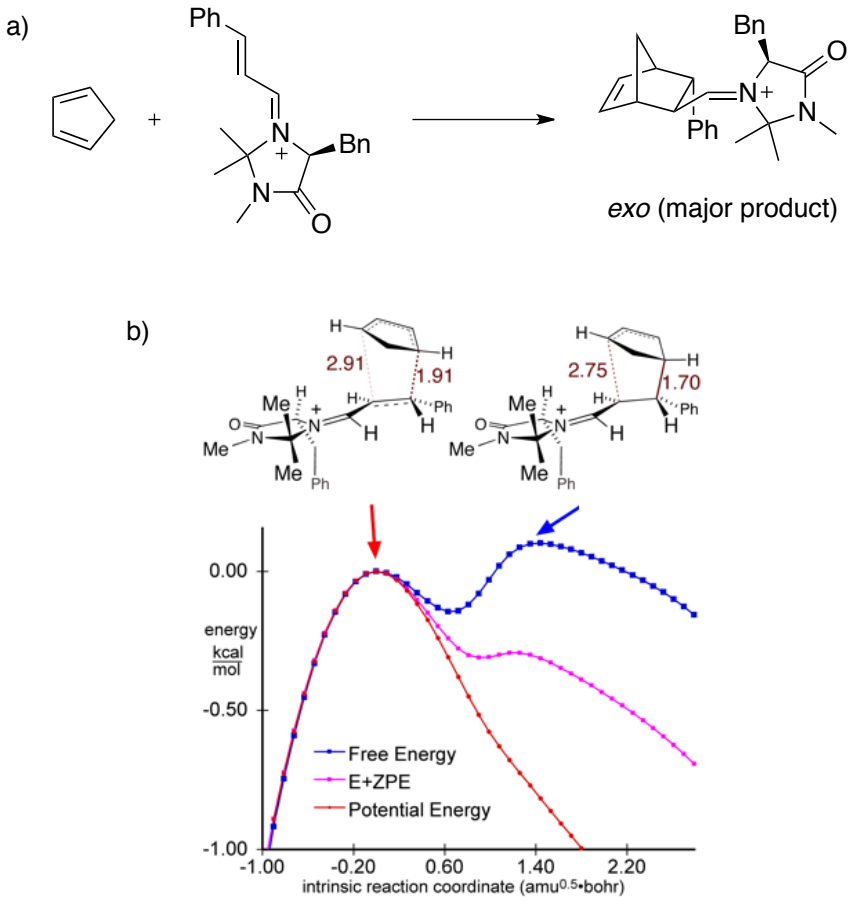


Figure 5 - 2: (a) Reaction of vinyliminium ion of *trans*-cinnamaldehyde. (b) Reaction coordinate for Diels-Alder cycloaddition of vinyliminium ion of *trans*-cinnamaldehyde[19]

Results and Discussion

With these exciting computational results, we sought to find a Diels-Alder reaction that will potentially show the formation of this entropic intermediate. The systems that seemed more promising were those that consisted of asymmetric dienophiles that contained an electron-withdrawing group reacting with symmetric dienes, such as cyclopentadiene or 1,3-butadiene. Also, we expected that systems for which the transitions states showed high asyncronicity were going to be the best candidates for this study.

With these ideas in mind, the first system to be studied was the reaction between 1,3-butadiene and 3-methy-2-methylenebutanal catalyzed by a Lewis acid (Figure 5 - 3). This reaction was studied via a combination of KIEs and computational calculations. The experimental KIEs were measured on two samples prepared from two independent reactions. The ^{13}C KIEs were measured at natural abundance on the product obtained from reactions taken to a 100 % conversion. Also, predicted KIEs were calculated from the frequencies of the located transition state, using QUIVER.

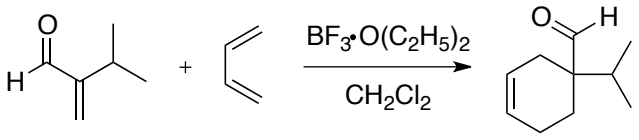


Figure 5 - 3: Lewis acid catalyzed Diels-Alder cycloaddition of 1,3-butadiene with 3-methy-2-methylenebutanal

The expected experimental result, in order to suggest the existence of recrossing in this reaction, was a ^{13}C KIE smaller than the predicted one by TST. Computationally, conventional transition state theory predicted a very asynchronous TS (TS located using B3LYP/6-31G*). At the TS the distance for the formation of the second C – C bond is quite large compared to the one corresponding to the first C – C bond formation (Figure 5 – 4).

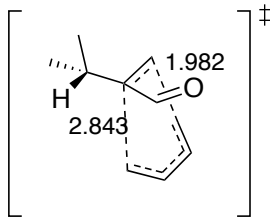


Figure 5 - 4: Transition state for the Diels-Alder cycloaddition of 1,3-butadiene with 3-methy-2-methylenebutanal

Due to the proximity of the carbon signals of interest in the 1D ^{13}C NMR it was necessary to convert the aldehyde product to its corresponding alcohol, in order to be able to measure the KIEs. To achieve this transformation the aldehyde was reduced to the alcohol using sodium borohydride. Finally, the KIEs were measured on the alcohol product (Table 5 – 1). Unfortunately, the results obtained experimentally matched very well with the predicted KIEs, showing that this was just an ordinary, asynchronous Diels-Alder cycloaddition.

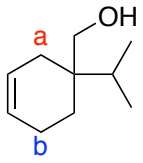


Table 5 - 1: Experimental and predicted KIEs for the lewis acid catalyzed Diels-Alder reaction of 1,3-butadiene with 3-methy-2-methylenebutanal

	Ratio	Experimental KIE	Predicted KIE[a]
b/a	0.978(5)	1.022(5)	1.027
	0.973(2)	1.028(2)	

[a] KIE was predicted by the QUIVER method based on the TS calculated using B3LYP/6-31G*

After this failing attempt of finding non-statistical recrossing, the same aldehyde was reacted with cyclopentadiene; however, we were not able to measure KIEs on the products because the reaction formed a mixture of inseparable *endo*- and *exo*- isomers, for which the signals corresponding to the carbons of interest overlapped. Some other aldehydes were also synthesized and reacted with cyclopentadiene; however, the same problem was encountered.

Due to the complications encountered with the reactions that involved symmetric dienes, we decided to rethink the systems that were going to be studied. After careful evaluation, we though that hetero Diels-Alder reactions were the best choice; specially, reactions of asymmetric dienes with dienophiles that contained a heteroatom. With this though, we decided to investigate the reaction between diene **1** and *p*-chlorobenzaldehyde (**2**) (Figure 5 – 5).[160]

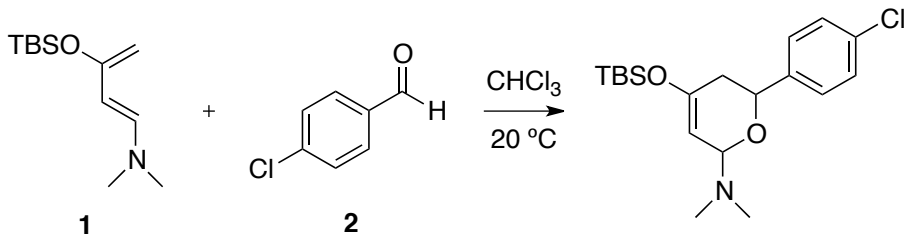


Figure 5 - 5: Hetero Diels-Alder cycloadition between diene **1** and *p*-chlorobenzaldehyde

In this case, we measured intermolecular KIEs on the *p*-chlorobenzaldehyde. In order to measure the KIEs, two independent reaction were taken to ~70 % conversion. The unreacted *p*-chlorobenzaldehyde (**2**) was recovered from the reaction mixture via column chromatography. The ^{13}C KIEs were measured at natural abundance on the recovered **2**, by comparing the isotopic composition of the sample with a standard made from material that was not submitted to the reaction conditions. The results are shown in Figure 5 – 6. The most interesting part of the experimental KIEs is that they are quite small for a Diels-Alder reaction, especially since the aldehyde carbon is involved in the cycloaddition.

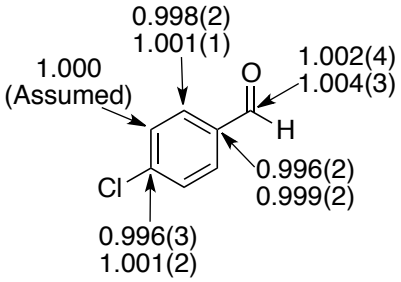


Figure 5 - 6: Intermolecular kinetic isotope effects for the hetero Diels-Alder reaction of **1** with *p*-chlorobenzaldehyde **2**

It has been proposed that for a system similar to the one under study, the reaction proceed via a stepwise process for which the formation of the C – C bond is the rate-limiting step.[161] In this work, the reaction was studied via computational calculations using B3LYP/6-31G*. With these preliminary results, we sought to try to predict the experimentally determined KIEs using the TS corresponding to the rate determining step. We started by locating the TS corresponding to the rate-limiting step, for the cycloaddition, using multiple computational methods, in addition to gas phase calculations and solvent models. The first calculation that we performed was using B3LYP/6-31+G** level in gas phase. As expected, the located TS was very asynchronous, almost like a stepwise process. Intrigued by this structure we decided to locate the TS for the reaction using two different solvent models, PCM and SMD. Interestingly, the same kind of TS structure was obtained using both solvent models.

With these results in hand, we located the TS corresponding to the C – C bond formation using other methods (B3LYP-D3 and M06-2X). Each of these calculations were performed using a chloroform PCM model. In addition, a TS including a $CHCl_3$

molecule was located, for each of the methods. Fortunately, all the located TS were very asynchronous, showing a C – C bond formation distance of 1.90 – 2.00 Å, and a C – O bond distance of 2.68 – 2.80 Å. Once the TSs were located, we proceeded to predict the KIEs using QUIVER. The results obtained from these predictions are shown in Figure 5 – 7.

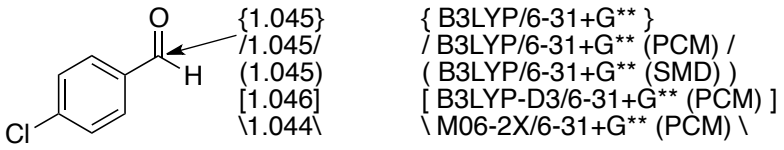


Figure 5 - 7: Predicted kinetic isotope effects for the hetero Diels-Alder reaction of diene **1** with *p*-chlorobenzaldehyde (**2**)

Interestingly, none of the predicted KIEs matched those observed experimentally. These results could indicate that the reaction is not a normal concerted Diels-Alder cycloaddition. Some possibilities that can explain the fact that TST cannot predict the KIEs are: a) the reaction is a stepwise process, for which the expected KIEs will be smaller if the second step was rate-limiting; or b) the reaction is affected by some dynamic effect that decreases the observed experimental KIE.

After careful consideration of each of the methods, and further validation against CCSD(T) calculations. It was decided that the method that best described the energetics of the system was M06-2X. With these results on hand, we proceeded to develop a POLYRATE calculation using the *endo*-TS located with M06-2X / 6-31+G** (PCM)

including an implicit $CHCl_3$ molecule. The results from this calculation showed that the rate limiting step was the formation of the C – C bond, followed by a long barrier-less rearrangement of the molecule to finally form the product.

Encouraged by the POLYRATE results, dynamic trajectories were started from the calculated TS using a PCM ($CHCl_3$) model and an explicit solvent molecule. A total of 198 trajectories were obtained. Interestingly, most of these trajectories recrossed to the starting materials (130 trajectories). In addition, a problem was encounter with some of the trajectories, around 17 of the results did not finished properly due to proton transfer from the $CHCl_3$ molecule to the O-atom of the aldehyde after the C – C bond formation.

In order to see if the proton transfer was real or if it was an underestimation of the barrier caused by M06-2X. A model system was studied using several different calculational methods. All of them showed that the proton transfer is not as facile as the M06-2X calculations showed, indicating that the trajectories showing the proton transfer did not represent what is happening in the reaction. These results support our hypothesis that the M06-2X calculations were underestimating the barrier for the proton transfer.

Up to this point, the experimental results in combination with computational calculations indicate that the reaction of *p*-chlorobenzaldehyde with diene **2** does not proceed via a typical asynchronous and concerted Diels-Alder cycloaddition. Additional high level calculations will need to be done in order to clearly understand the mechanistic pathway of the reaction.

Future Work

Additional calculations are in progress in order to fully understand the mechanism of the reaction. Additional molecular dynamics simulations to avoid the unreal proton transfer from the $CHCl_3$ molecule are currently been pursued. In addition, calculations to find a VTS that can account for the experimentally observed KIEs are in progress. All of these results together, will allow us to understand the mechanistic pathway, and the dynamic effects involve in the Diels-Alder cycloaddition of diene **1** with *p*-chlorobenzaldehyde.

Experimental and Computational Procedures

Synthesis of 3-methyl-2-methylenebutanal.[162] A mixture of aqueous formaldehyde (37 % formaldehyde in water, 1.89 g, 23.22 mmol) and isovaleraldehyde (2.00 g, 23.22 mmol) in 2.32 mL of isopropanol (10 M) was added propionic acid (0.17 g, 2.32 mmol) and pyrrolidine (0.16 g, 2.32 mmol), was stirred at 45 ºC for 4 h in a sealed tube. The reaction was quenched by the addition of a $NaHCO_3$ saturated solution. The mixture was extracted with CH_2Cl_2. The organics were washed with brine, dried over Na_2SO_4, and concentrated in vacuum. The compound was used without further purification. ^{1}H NMR ($CDCl_3$, 500 MHz): ∂ 9.87 (s, 1 H), 6.41 (s, 1 H), 6.08 (s, 1 H), 2.58 (m, *J*=6.8 Hz, 1 H), 1.06 (d, *J*=6.8 Hz, 6 H).

Synthesis of 1-isopropylcyclohex-3-enecarbaldehyde. A mixture of 3-methyl-2-methylenebutanal (1.00 g, 9.98 mmol) in 20.00 mL of dichloromethane (0.5 M), under N_2 atmosphere, was cooled to -10 ºC. Boron trifluoride diethyl etherate (0.71 g, 4.99

mmol) was then added carefully. After stirring for a couple of minutes, the 1,4-butadiene (1.08 g, 19.97 mmol) was bubbled into the solution. The reaction mixture was left stirring at -10 ºC for 4.5 h. Reaction was stopped by addition of a 1M HCl solution until pH ~ 7. The phases were separated; and the organic layer was washed with a saturated $NaHCO_3$ solution, brine, dried over Na_2SO_4 and concentrated under vacuum. Product was purified via flash column chromatography using 4% ethyl acetate in hexanes.

Synthesis of (1-isopropylcyclohex-3-en-1-yl)methanol. A solution of 1-isopropylcyclohex-3-enecarbaldehyde (0.70 g, 4.54 mmol) in 9.08 mL of methanol (0.5 M) was cooled to 0 ºC. Then the sodium boron hydride (0.17 g, 4.54 mmol) was added slowly. Reaction's progress was followed by TLC and ^{1}H NMR. Excess sodium boron hydride was quenched by addition of a 1M HCl solution until pH ~ 6. The mixture was extracted with diethyl ether. The combined extracts were washed with water and brine, dried over $MgSO_4$ and concentrated under vacuum. Product was purified via flash column chromatography using 15 % ethyl acetate in hexanes. ^{13}C NMR ($CDCl_3$, 125.81 MHz): ∂ 126.20, 125.57, 63.72, 37.62, 30.94, 28.26, 25.60, 22.26, 16.92, 16.63.

Synthesis of (E)-4-dimethylamino-3 butene-2-one.[163] A mixture of 20.1 mL of the acetylacetaldehyde dimethyl acetal (20.00 g, 0.15 mol) and a 2.0 M solution of dimethylamine in methanol (85 mL, 0.17 mol) was left stirring at room temperature for 4 hours. The reaction mixture was concentrated under vaccum and the resulting oil was purified via vacuum distillation (0.25 mm, 120 ºC). The collection flask was cooled with ice as soon as product started to distill. The product was collected as a pale-orange oil, with a yield of 15.35 g (88 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) ∂: 2.10 (s, 3H), 2.88

(br s, 3H), 2.99 (br s, 3H), 5.05 (d, 1H, J=12.8), 7.47 (d, 1H, J=12.8); ^{13}C NMR (75 MHz, $CDCl_3$) ∂: 28.0, 36.9, 44.5, 96.6, 152.6, 195.2

Synthesis of (E)-1-dimethylamono-3-tert-butyldimethylsiloxy-1,3-butadiene.[163] A solution 1.0 M solution of sodium bis(trimethylsilyl)amide (NaHMDS) in THF (171.3 mL, 171.3 mmol) cooled to -78 ºC, under nitrogen atmosphere. After a yeloow-white suspention was formed, a solution of (*E*)-4-dimethylamino-3-butene-2-one (15.18 g, 131.8 mmol) in THF (66 mL) was added dropwise via an addition funnel. After the addition, the reaction mixture was left stirring for an additional 1.0 h at -78 ºC. Then, a solution of tert-butylchlorodimethylsilane (25.82 g, 171.3 mmol) in THF (82 mL) was added dropwise via an addition funnel. After the addition, the cooling bath was removed and the reaction mixture was left stirring until it reached room temperature (~1.5 h). The solution was then poured into 600 mL of anhydrous diethylether. The resulting suspention was allowed to stand for 30 mins and then suction filtered through a pad of Celite (Celite 545). The filter cake was washed with diethylether, and the filtrate was concentrated under vacuum. The resulting dark orange oil was purified via vacuum distillation (0.3 mm, 120 ºC). The collection flask was cooled with ice as soon as product started to distill. The product was collected as a light-yellow oil, with a yield of 26.16 g (44 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) ∂: 0.19 (s,6H), 0.98 (s, 9H), 2.70 (s, 6 H), 3.84 (s, 1H), 3.92 (s, 1H), 4.78 (d, 1H, J=13.2), 6.57(d,1H, J=13.2); ^{13}C NMR (75 MHz, $CDCl_3$) ∂: -4.6, 18.3, 25.9, 40.5, 85.8, 95.9, 140.9, 156.4

*Diels-Alder cycloaddition of diene **1** with p-chlorobenzaldehyde **2**.*[160] The diene **1** (9.00 g, 28.9 mmol) was added dropwise to a solution of *p*-chlorobenzaldehyde (**2**) (5.80

g, 41.3 mmol) in 83.0 mL of $CHCl_3$ (0.5 M). The reaction was monitored by ^1H NMR until **1** was consumed, which took approximatelly 16 h.After the reaction was done, the mixture was concentrated under vacuum. The unreacted **2** was recovered via column chromatography using silica and 10 % ethyl acetate in hexanes.

KIE determination for p-chlorobenzaldehyde NMR samples. All NMR samples consisted of approximately 240 mg of the *p*-chlorobenzaldehyde in 5 mm NMR tubes filled to a constant height of 5 cm with d_8-THF. The ^{13}C spectra were recorded at 125.51 MHz using inverse gated decoupling, 173.2 s delays between calibrated $\pi/2$ pulses, and 8 s acquisition time. The 173.2 s delay was based on the T1 of the signal at 190.1 ppm, which was measured to be 28.86 s. Integrations were numerically determined using a constant integration region for each peak. A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction was ever applied. A total number of 6 spectra were recorded for each sample and standard. The integration value of each peak was determined by the average of all measurements. The uncertainty of the measurements was determined by considering a two-side 95 % confidence interval in a T-distribution.

KIE determination for (1-isopropylcyclohex-3-en-1-yl)methanol NMR samples. All NMR samples consisted of approximately 290 mg of the alcohol product in 5 mm NMR tubes filled to a constant height of 5 cm with $CDCl_2$. The ^{13}C spectra were recorded at 125.51 MHz using inverse gated decoupling, 8.64 s delays between calibrated $\pi/2$ pulses, and 5 s acquisition time. The 8.64 s delay was based on the T1 of the signal at 20.3 ppm, which was measured to be 1.44 s. Integrations were numerically

determined using a constant integration region for each peak. A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction was ever applied. A total number of 6 spectra were recorded for each sample. The integration value of each peak was determined by the average of all measurements. The uncertainty of the measurements was determined by the standard deviation of the 6 measurements.

General computational procedure. Calculations of structures, energies, and frequencies employed default procedures in Gaussian09 unless otherwise noted. Complete structures and energetics are provided in Appendix B. All absolute energies are in Hartrees. All relative energies are presented in kcal/mol.

KIE predictions. For the various transition structures calculated, conventional TST isotope effects were calculated by the method of Bigeleisen and Mayer using the program QUIVER, modified for easier use with Gaussian 09 and compilation on modern compilers. The conventional TST isotope effects were then corrected by a one-dimensional infinite-parabola tunneling correction. For simplicity, we have adopted the practice of using a single frequency scaling factor of 0.9614 in all cases. Within a reasonable range, the choice of scaling factor has a negligible effect on the predicted value of any small ^{13}C KIE and it affects large ^{13}C KIEs by no more than 0.002. We note that the applicability of any particular literature scaling factor to carbon isotope effects is questionable.

CHAPTER VI

CONCLUSIONS

The understanding of the mechanism of organic reactions is of huge importance for the development of new synthetic methods. Physical organic chemists have developed multiple approaches to try to understand the behavior of organic reactions. Through this dissertation we employed a combination of experimental and computational studies in order to achieve this goal. Several experimental approaches were used depending on the nature of the reaction under study. The experimental studies included: determination of product ratios by ^{1}H NMR, and determination of inter- and intramolecular KIEs at natural abundance using ^{13}C NMR. Computational calculations were used in order to understand the experimental results, and in order to elucidate specific mechanistic details about the reactions studied.

The solvent dynamics affecting the product selectivity in the nitration of toluene, using NO_2BF_4 in CH_2Cl_2, shows the importance of an explicit solvent model when performing computational calculations. For this reaction we showed how the reorganization of the solvent and the counter ion will influence the selectivity when highly reactive electrophiles are involved. In addition, our findings show the inability of TST to explain the selectivity of this kind of reaction. These findings change completely the perspective of the use of TSs in order to understand the mechanism of a reaction that involves very reactive electrophiles.

Interestingly, the nitration of toluene does not represent the only electrophilic aromatic substitution that is affected by a dynamic effect. Here we showed how the Friedel-Crafts acylation of very reactive aromatic ethers are affected by a bifurcation in the selectivity of the reacting aromatic carbon. The KIEs obtained for these reactions were inconsistent with the conventional mechanism, and they implicate dynamic control of the regioselectivity subsequent to the rate-limiting step. Computational studies were employed to support this idea. The results showed that the reaction was governed by an early, symmetrical and rate-limiting TS followed by desymmetrization of trajectories on a bifurcating energy surface.

In the case of the Cope-type hydroamination of alkynes, TST could actually account for the experimental results. Showing that the reaction, indeed, happens via a 5-membered ring TS to obtain a good selectivity for the addition at the internal carbon of the alkyne. In addition, our computational studies showed how the structure of the TS can affect the observed KIEs. As explained before, the distances for the C – N and C – H bonds had a correlation with the predicted KIEs. The results prove the importance of KIEs when trying to understand the structure of a TS for a determined reaction.

Preliminary computational studies suggested that the Diels-Alder reaction of cyclopentadiene and *trans*-cinnamaldehyde could be affected by non-statistical recrossing. Encouraged by these results we sought to find a Diels-Alder reaction that showed a very asynchronous TS. The reason for looking a system with this characteristic was that a seemingly concerted reaction that involves an asynchronous TS, in the potential energy surface, could show a second barrier for the formation of the "second"

bond to finally form the product, in the free energy surface. Experimental KIEs were measured in several Diels-Alder reactions. Fortunately, the Diels-Alder cycloaddition of *(E)*-1-dimethylamono-3-tert-butyldimethylsiloxy-1,3-butadiene with *p*-chlorobenzaldehyde seem to be affected by non-statistical recrossing. Computational studies are in process to fully understand the extent of recrossing affecting the reaction, the structure of the intermediate, and the subsequent rate-limiting TS.

In conclusion, a combination of experimental KIEs and/or product ratio determinations, in combination with computational calculations has been employed to study a series of organic reactions. We have shown how experimental and computational studies, when used in conjunction, can be used for the accurate elucidation and understanding of mechanistic details of organic reactions.

REFERENCES

(1) Hill, R. K.; Conley, R. T.; Chortyk, O. T. *J. Am. Chem. Soc.* **1965,** *87*, 5646-5651.

(2) Burgstahler, A. W.; Chien, P.-L. *J. Am. Chem. Soc.* **1964,** *86*, 2940-2941.

(3) Mylonakis, S. G.; Seltzer, S. *J. Am. Chem. Soc.* **1968,** *90*, 5487-5489.

(4) Raaen, V. F.; Juhlke, T.; Brown, F. J.; Collins, C. J. *J. Am. Chem. Soc.* **1974,** *96*, 5928-5930.

(5) Beak, P.; Berger, K. R. *J. Am. Chem. Soc.* **1980,** *102*, 3848-3856.

(6) Parkin, D. W.; Schramm, V. L. *Biochemistry* **1987,** *26*, 913-920.

(7) Butler, G. B.; Angelo, R. J. *J. Am. Chem. Soc.* **1955,** *77*, 1767-1769.

(8) Cohen, T.; Deets, G. L. *J. Am. Chem. Soc.* **1967,** *89*, 3939-3940.

(9) Bernasconi, C. F.; Sun, W. *J. Am. Chem. Soc.* **2002,** *124*, 2299-2304.

(10) Sikowitz, M. D.; Shome, B.; Zhang, Y.; Begley, T. P.; Ealick, S. E. *Biochemistry* **2013,** *52*, 7830-7839.

(11) Campbell, D. O.; Kilpatrick, M. L. *J. Am. Chem. Soc.* **1954,** *76*, 893-901.

(12) Morgan, M. S.; Cretcher, L. H. *J. Am. Chem. Soc.* **1948,** *70*, 375-378.

(13) Zhang, X.; Romero, A.; Foote, C. S. *J. Am. Chem. Soc.* **1993,** *115*, 11024-11025.

(14) Biswas, B.; Collins, S. C.; Singleton, D. A. *J. Am. Chem. Soc.* **2014,** *136*, 3740-3743.

(15) Mageswaran, S.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc. Perk. Trans. 1* **1981**, 1953-1962.

(16) Evans, M. G.; Polanyi, M. *Trans. Far. Soc.* **1935,** *31*, 875-894.

(17) Eyring, H. *J. Chem Phys.* **1935,** *3*, 107-115.

(18) Chen, Z.; Nieves-Quinones, Y.; Waas, J. R.; Singleton, D. A. *J. Am. Chem. Soc.* **2014,** *136*, 13122-13125.

(19) Gonzalez-James, O. M.; Kwan, E. E.; Singleton, D. A. *J. Am. Chem. Soc.* **2012,** *134*, 1914-1917.

(20) Andujar-De Sanctis, I. L.; Singleton, D. A. *Org. Lett.* **2012,** *14*, 5238-5241.

(21) Bogle, X. S.; Singleton, D. A. *Org. Lett.* **2012,** *14*, 2528-2531.

(22) Oyola, Y.; Singleton, D. A. *J. Am. Chem. Soc.* **2009,** *131*, 3130-3131.

(23) Quijano, L. M. M.; Singleton, D. A. *J. Am. Chem. Soc.* **2011,** *133*, 13824-13827.

(24) Doubleday, C. *J. Phys. Chem. A* **2001,** *105*, 6333-6341.

(25) Doubleday, C.; Li, G.; Hase, W. L. *Phys. Chem. Chem. Phys.* **2002,** *4*, 304-312.

(26) Ussing, B. R.; Hang, C.; Singleton, D. A. *J. Am. Chem. Soc.* **2006,** *128*, 7594-7607.

(27) Wang, Z.; Hirschi, J. S.; Singleton, D. A. *Angew. Chem. Int. Ed.* **2009,** *48*, 9156-9159.

(28) Bender, M. L.; Hoeg, D. F. *J. Am. Chem. Soc.* **1957,** *79*, 5649-5654.

(29) Beno, B. R.; Houk, K. N.; Singleton, D. A. *J. Am. Chem. Soc.* **1996,** *118*, 9984-9985.

(30) Francisco, W. A.; Abu-Soud, H. M.; DelMonte, A. J.; Singleton, D. A.; Baldwin, T. O.; Raushel, F. M. *Biochemistry* **1998,** *37*, 2596-2606.

(31) Kresge, A. J.; Lichtin, N. N.; Rao, K. N. *J. Am. Chem. Soc.* **1963,** *85*, 1210-1211.

(32) Mislow, K.; Graeve, R.; Gordon, A. J.; Wahl, G. H. *J. Am. Chem. Soc.* **1963,** *85*, 1199-1200.

(33) Schneider, F. W.; Rabinovitch, B. S. *J. Am. Chem. Soc.* **1963,** *85*, 2365-2370.

(34) Singleton, D. A.; Thomas, A. A. *J. Am. Chem. Soc.* **1995,** *117*, 9357-9358.

(35) Merrigan, S. R.; Le Gloahec, V. N.; Smith, J. A.; Barton, D. H. R.; Singleton, D. A. *Tet. Lett.* **1999,** *40*, 3847-3850.

(36) Wong, K.-Y.; Gu, H.; Zhang, S.; Piccirilli, J. A.; Harris, M. E.; York, D. M. *Angew. Chem. Int. Ed.* **2012,** *51*, 647-651.

(37) Liu, Z.; Yamamichi, H.; Madrahimov, S. T.; Hartwig, J. F. *J. Am. Chem. Soc.* **2011,** *133*, 2772-2782.

(38) Anderson, M. A.; Cleland, W. W.; Huang, D. T.; Chan, C.; Shojaei, M.; Christopherson, R. I. *Biochemistry* **2006,** *45*, 7132-7139.

(39) Anding, B. J.; Ellern, A.; Woo, L. K. *Organometallics* **2012,** *31*, 3628-3635.

(40) Tormos, J. R.; Wiley, K. L.; Wang, Y.; Fournier, D.; Masson, P.; Nachon, F.; Quinn, D. M. *J. Am. Chem. Soc.* **2010,** *132*, 17751-17759.

(41) Bigeleisen, J.; Mayer, M. G. *J. Chem Phys.* **1947,** *15*, 261-267.

(42) Olah, G. A.; Kuhn, S. J.; Flood, S. H.; Evans, J. C. *J. Am. Chem. Soc.* **1962,** *84*, 3687-3693.

(43) Olah, G. A.; Kuhn, S. J.; Flood, S. H. *J. Am. Chem. Soc.* **1961,** *83*, 4581-4585.

(44) Olah, G. A.; Kuhn, S. J. *J. Am. Chem. Soc.* **1962,** *84*, 3684-3687.

(45) Olah, G. A.; Kuhn, S. J.; Flood, S. H. *J. Am. Chem. Soc.* **1961,** *83*, 4571-4580.

(46) Olah, G. A.; Narang, S. C.; Olah, J. A. *Procc. Nat. Acad. Sci.* **1981,** *78*, 3298-3300.

(47) Olah, G. A. *Acc. Chem. Res.* **1971,** *4*, 240-248.

(48) Ridd, J. H. *Acc. Chem. Res.* **1971,** *4*, 248-253.

(49) Stock, L. *Prog. Phys. Org. Chem.* **1976,** *12*, 21-47.

(50) Olah, G. A.; Lin, H. C.; Olah, J. A.; Narang, S. C. *Procc. Nat. Acad. Sci.* **1978,** *75*, 545-548.

(51) Santiago, C.; Houk, K. N.; Perrin, C. L. *J. Am. Chem. Soc.* **1979,** *101*, 1337-1340.

(52) DeHaan, F. P.; Covey, W. D.; Delker, G. L.; Baker, N. J.; Feigon, J. F.; Miller, K. D.; Stelter, E. D. *J. Am. Chem. Soc.* **1979,** *101*, 1336-1337.

(53) Olah, G. A.; Narang, S. C.; Olah, J. A.; Lammertsma, K. *Procc. Nat. Acad. Sci.* **1982,** *79*, 4487-4494.

(54) Kenner, J.; Kenner *Nature* **1945,** *156*, 369-370.

(55) Pedersen; Pedersen, E. B.; Petersen, T. E.; Torssell, K.; Lawesson, S. O. *Tetrahedron* **1973,** *29*, 579-584.

(56) Perrin, C. L. *J. Am. Chem. Soc.* **1977,** *99*, 5516-5518.

(57) Todres; Todres, Z. V. *Tetrahedron* **1985,** *41*, 2771-2823.

(58) Kochi, J. K. *Adv. Free Rad. Chem.* **1990,** *1*, 53-119.

(59) Sankararaman, S.; Kochi, J. K. *J. Chem. Soc. Pek. Trans. 2* **1991,** *1*, 1-12.

(60) Rathore, R.; Kochi, J. K. *Adv. Phys. Org. Chem.* **2000,** *35*, 193-318.

(61) Kochi, J. K. *Angew. Chem. Int. Ed. Engl.* **1988,** *27*, 1227-1266.

(62) Kochi, J. K. *Acc. Chem. Res.* **1992,** *25*, 39-47.

(63) Johnston, J. F.; Ridd, J. H.; Sandal, J. P. B. *Chem. Commun.* **1989**, 244-246.

(64) Eberson, L.; Radner, F. *Acc. Chem. Res.* **1987,** *20*, 53-59.

(65) Lund, T.; Eberson, L. *J. Chem. Soc. Perk. Trans. 2* **1997**, 1435-1444.

(66) Koleva, G.; Galabov, B.; Wu, J. I.; Schaefer Iii, H. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2009,** *131*, 14722-14727.

(67) Kim, E. K.; Lee, K. Y.; Kochi, J. K. *J. Am. Chem. Soc.* **1992,** *114*, 1756-1770.

(68) Koleva, G.; Galabov, B.; Hadjieva, B.; Schaefer, H. F.; Schleyer, P. v. R. *Angew. Chem. Int. Ed.* **2015,** *54*, 14123-14127.

(69) Hubig, S. M.; Kochi, J. K. *J. Org. Chem.* **2000,** *65*, 6807-6818.

(70) Gilbert, T. M. *J. Phys. Chem. A* **2004,** *108*, 2550-2554.

(71) Kelly, K. K.; Hirschi, J. S.; Singleton, D. A. *J. Am. Chem. Soc.* **2009,** *131*, 8382-8383.

(72) Thomas, J. B.; Waas, J. R.; Harmata, M.; Singleton, D. A. *J. Am. Chem. Soc.* **2008,** *130*, 14544-14555.

(73) Singleton, D. A.; Hang, C.; Szymanski, M. J.; Greenwald, E. E. *J. Am. Chem. Soc.* **2003,** *125*, 1176-1177.

(74) González-Lafont, À.; Moreno, M.; Lluch, J. M. *J. Am. Chem. Soc.* **2004,** *126*, 13089-13094.

(75) Zheng, J.; Papajak, E.; Truhlar, D. G. *J. Am. Chem. Soc.* **2009,** *131*, 15754-15760.

(76) Fischer, A.; Vaughan, J.; Wright, G. J. *J. Chem. Soc. B* **1967**, 368-372.

(77) Fischer, A.; Wright, G. J. *Aust. J. Chem.* **1974,** *27*, 217-9.

(78) Rai, S. N.; Truhlar, D. G. *J. Chem. Phys.* **1983,** *79*, 6049-6059.

(79) Plata, R. E.; Singleton, D. A. *J. Am. Chem. Soc.* **2015,** *137*, 3811-3826.

(80) Kumar, S.; Rosenberg, J. M.; Bouzida, D.; Swendsen, R. H.; Kollman, P. A. *J. Comp. Chem.y* **1992,** *13*, 1011-1021.

(81) Moodie, R. B.; Schofield, K. *Acc. Chem. Res.* **1976,** *9*, 287-292.

(82) Barnes, C. E.; Myhre, P. C. *J. Am. Chem. Soc.* **1978,** *100*, 975-976.

(83) Fawcett, W. R.; Foss, C. A. J. *Electrochim. Acta* **1991,** *36*, 1767-1774.

(84) Hunger, J.; Stoppa, A.; Thoman, A.; Walther, M.; Buchner, R. *Chem. Phys. Lett.* **2009,** *471*, 85-91.

(85) Coombes, R. G.; Moodie, R. B.; Schofield, K. *J. Chem. Soc. B* **1968**, 800-804.

(86) Truhlar, D. G., *Isotope Effects in Chemistry and Biology*. Kohen, A. Limbach, H. ed.; Marcel Dekker: New York, 2006; p 579-620.

(87) Koleva, G.; Galabov, B.; Kong, J.; Schaefer, H. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2011,** *133*, 19094-19101.

(88) Skokov, S.; Wheeler, R. A. *J. Phys. Chem. A* **1999,** *103*, 4261-4269.

(89) Gwaltney, S. R.; Rosokha, S. V.; Head-Gordon, M.; Kochi, J. K. *J. Am. Chem. Soc.* **2003,** *125*, 3273-3283.

(90) Brown, H. C.; Nelson, K. L. *J. Am. Chem. Soc.* **1953,** *75*, 6292-6299.

(91) McGary, C. W.; Okamoto, Y.; Brown, H. C. *J. Am. Chem. Soc.* **1955,** *77*, 3037-3043.

(92) Brown, H. C.; Jungk, H. *J. Am. Chem. Soc.* **1956,** *78*, 2182-2184.

(93) Brown, H. C.; Jungk, H. *J. Am. Chem. Soc.* **1955,** *77*, 5584-5589.

(94) Brown, H. C.; Smoot, C. R. *J. Am. Chem. Soc.* **1956,** *78*, 6255-6259.

(95) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1957,** *79*, 1913-1917.

(96) Brown, H. C.; Young, H. L. *J. Org. Chem.* **1957,** *22*, 719-723.

(97) Brown, H. C.; Jensen, F. R. *J. Am. Chem. Soc.* **1958,** *80*, 2291-2296.

(98) Jensen, F. R.; Marino, G.; Brown, H. C. *J. Am. Chem. Soc.* **1959,** *81*, 3303-3307.

(99) Brown, H. C.; Marino, G.; Stock, L. M. *J. Am. Chem. Soc.* **1959,** *81*, 3310-3314.

(100) Valtazanos, P.; Ruedenberg, K. *Theoretica chimica acta* **1986,** *69*, 281-307.

(101) Zhou, C.; Birney, D. M. *Org. Lett.* **2002,** *4*, 3279-3282.

(102) Caramella, P.; Quadrelli, P.; Toma, L. *J. Am. Chem. Soc.* **2002,** *124*, 1130-1131.

(103) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992,** *114*, 5879-5881.

(104) Mann, D. J.; Hase, W. L. *J. Am. Chem. Soc.* **2002,** *124*, 3208-3209.

(105) Singleton, D. A.; Hang, C.; Szymanski, M. J.; Meyer, M. P.; Leach, A. G.; Kuwata, K. T.; Chen, J. S.; Greer, A.; Foote, C. S.; Houk, K. N. *J. Am. Chem. Soc.* **2003,** *125*, 1319-1328.

(106) Bekele, T.; Christian, C. F.; Lipton, M. A.; Singleton, D. A. *J. Am. Chem. Soc.* **2005,** *127*, 9216-9223.

(107) Çelebi-Ölçüm, N.; Ess, D. H.; Aviyente, V.; Houk, K. N. *J. Am. Chem. Soc.* **2007,** *129*, 4528-4529.

(108) Hammond, G. S. *J. Am. Chem. Soc.* **1955,** *77*, 334-338.

(109) Darbeau, R. W.; White, E. H. *J. Org. Chem.* **2000,** *65*, 1121-1131.

(110) DeHaan, F. P.; Djaputra, M.; Grinstaff, M. W.; Kaufman, C. R.; Keithly, J. C.; Kumar, A.; Kuwayama, M. K.; Macknet, K. D.; Na, J.; Patel, B. R.; Pinkerton, M. J.; Tidwell, J. H.; Villahermosa, R. M. *J. Org. Chem.* **1997,** *62*, 2694-2703.

(111) Olah, G. A.; Olah, J. A.; Ohyama, T. *J. Am. Chem. Soc.* **1984,** *106*, 5284-5290.

(112) Darbeau, R.; Darbeau; Siso, L.; Trahan, G.; Nolan, R. *Lett. Org. Chem.* **2005,** *2*, 139-144.

(113) Draper, M. R.; Ridd, J. H. *J. Chem. Soc. Chem. Comm.* **1978**, 445-446.

(114) Zhu, H.; Meyer, M. P. *Chem. Comm.* **2011,** *47*, 409-411.

(115) Rys, P.; Skrabal, P.; Zollinger, H. *Angew. Chem. Int. Ed.* **1972,** *11*, 874-883.

(116) Buckley, T. F.; Rapoport, H. *J. Am. Chem. Soc.* **1980,** *102*, 3056-3062.

(117) Singleton, D. A.; Szymanski, M. J. *J. Am. Chem. Soc.* **1999,** *121*, 9455-9456.

(118) Singleton, D. A.; Schulmeier, B. E. *J. Am. Chem. Soc.* **1999,** *121*, 9313-9317.

(119) Denney, D. B.; Klemchuk, P. P. *J. Am. Chem. Soc.* **1958,** *80*, 6014-6016.

(120) Olah, G. A.; Kuhn, S. J.; Flood, S. H.; Hardie, B. A. *J. Am. Chem. Soc.* **1964,** *86*, 2203-2209.

(121) Suzukawa, H.; Wolfsberg, M.; Thompson, D. *J. Chem Phys.* **1978,** *68*, 455-472.

(122) Hase, W.; Kihyung, S.; Gordon, M. S. *Comp. Sci. Eng.* **2003,** *5*, 36-44.

(123) Hase, W. L. *J. Phys. Chem.* **1986,** *90*, 365-374.

(124) Olah, G. A.; Moffatt, M. E.; Kuhn, S. J.; Hardie, B. A. *J. Am. Chem. Soc.* **1964,** *86*, 2198-2202.

(125) Corriu, R.; Corriu *Tetrahedron* **1971,** *27*, 5819-5831.

(126) Corriu, R.; Corriu *Tetrahedron* **1971,** *27*, 5601-5618.

(127) Wolfsberg, M. *Acc. Chem. Res.* **1972,** *5*, 225-233.

(128) Saunders, M.; Laidig, K. E.; Wolfsberg, M. *J. Am. Chem. Soc.* **1989,** *111*, 8989-8994.

(129) Bell, R. P., *The Tunnel Effect in Chemistry*. Chapman & Hall: London, 1980.

(130) Meyer, M. P.; DelMonte, A. J.; Singleton, D. A. *J. Am. Chem. Soc.* **1999,** *121*, 10865-10874.

(131) DelMonte, A. J.; Haller, J.; Houk, K. N.; Sharpless, K. B.; Singleton, D. A.; Strassner, T.; Thomas, A. A. *J. Am. Chem. Soc.* **1997,** *119*, 9907-9908.

(132) Singleton, D. A.; Merrigan, S. R.; Liu, J.; Houk, K. N. *J. Am. Chem. Soc.* **1997,** *119*, 3385-3386.

(133) Dai, S.-H.; Dolbier, W. R. *J. Am. Chem. Soc.* **1972,** *94*, 3946-3952.

(134) Grdina, M. B.; Orfanopoulos, M.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979,** *101*, 3111-3112.

(135) Metiu, H.; Ross, J.; Silbey, R.; George, T. F. *J. Chem Phys.* **1974,** *61*, 3200-3209.

(136) Shustov, G. V.; Liu, M. T. H.; Houk, K. N. *Can. J. Chem.* **1999,** *77*, 540-549.

(137) Morgan, S.; Jackson, J. E.; Platz, M. S. *J. Am. Chem. Soc.* **1991,** *113*, 2782-2783.

(138) Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984,** *106*, 4293-4294.

(139) Wong; Wong, P. C.; Griller, D.; Scaiano, J. C. *Chem. Phys. Lett.* **1981,** *83*, 69-72.

(140) Turro, N. J.; Lehr, G. F.; Butcher, J. A.; Moss, R. A.; Guo, W. *J. Am. Chem. Soc.* **1982,** *104*, 1754-1756.

(141) Moss; Moss, R. A.; Perez, L. A.; Turro, N. J.; Gould, I. R.; Hacker, N. P. *Tet. Lett.* **1983,** *24*, 685-688.

(142) Mader, E. A.; Larsen, A. S.; Mayer, J. M. *J. Am. Chem. Soc.* **2004,** *126*, 8066-8067.

(143) de Sainte Claire, P.; Peslherbe, G. H.; Wang, H.; Hase, W. L. *J. Am. Chem. Soc.* **1997,** *119*, 5007-5012.

(144) Hase, W. L.; Wardlaw, D. M., Bimolecular Collisions. In *Bimolecular Collisions*, Baggot, J. E.; Ashfold, M. N., Eds. Burlington House: London, 1989.

(145) Lei, W.; Zhang, R.; McGivern, W. S.; Derecskei-Kovacs, A.; North, S. W. *J. Phys. Chem. A* **2001,** *105*, 471-477.

(146) Müller, T. E.; Hultzsch, K. C.; Yus, M.; Foubelo, F.; Tada, M. *Chem. Rev.* **2008,** *108*, 3795-3892.

(147) Müller, T. E.; Beller, M. *Chem. Rev.* **1998,** *98*, 675-704.

(148) Moran, J.; Gorelsky, S. I.; Dimitrijevic, E.; Lebrun, M.-E.; Bédard, A.-C.; Séguin, C.; Beauchemin, A. M. *J. Am. Chem. Soc.* **2008,** *130*, 17893-17906.

(149) Cooper, N. J.; Knight, D. W. *Tetrahedron* **2004,** *60*, 243-269.

(150) Komaromi, I.; Tronchet, J. M. J. *J. Phys. Chem. A* **1997,** *101*, 3554-3560.

(151) Acevedo, O.; Jorgensen, W. L. *J. Am. Chem. Soc.* **2006,** *128*, 6141-6146.

(152) Krenske, E. H.; Davison, E. C.; Forbes, I. T.; Warner, J. A.; Smith, A. L.; Holmes, A. B.; Houk, K. N. *J. Am. Chem. Soc.* **2012,** *134*, 2434-2441.

(153) Ciganek, E.; Read, J. M.; Calabrese, J. C. *J. Org. Chem.* **1995,** *60*, 5795-5802.

(154) Johns, A. M.; Sakai, N.; Ridder, A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006,** *128*, 9306-9307.

(155) Zhao, S.-B.; Bilodeau, E.; Lemieux, V.; Beauchemin, A. M. *Org. Lett.* **2012,** *14*, 5082-5085.

(156) Holmes, H. L., The Diels-Alder Reaction Ethylenic and Acetylenic Dienophiles. In *Organic Reactions*, John Wiley & Sons, Inc.: 2004.

(157) Nicolaou, K. C.; Snyder, S. A.; Montagnon, T.; Vassilikogiannakis, G. *Angew. Chem. Int. Ed.* **2002,** *41*, 1668-1698.

(158) Singleton, D. A.; Schulmeier, B. E.; Hang, C.; Thomas, A. A.; Leung, S.-W.; Merrigan, S. R. *Tetrahedron* **2001,** *57*, 5149-5160.

(159) Kanaan, N.; Ferrer, S.; Martí, S.; Garcia-Viloca, M.; Kohen, A.; Moliner, V. *J. Am. Chem. Soc.* **2011,** *133*, 6692-6702.

(160) Huang, Y.; Rawal, V. H. *Org. Lett.* **2000,** *2*, 3321-3323.

(161) Domingo, L. R.; Andrés, J. *J. Org. Chem.* **2003,** *68*, 8662-8668.

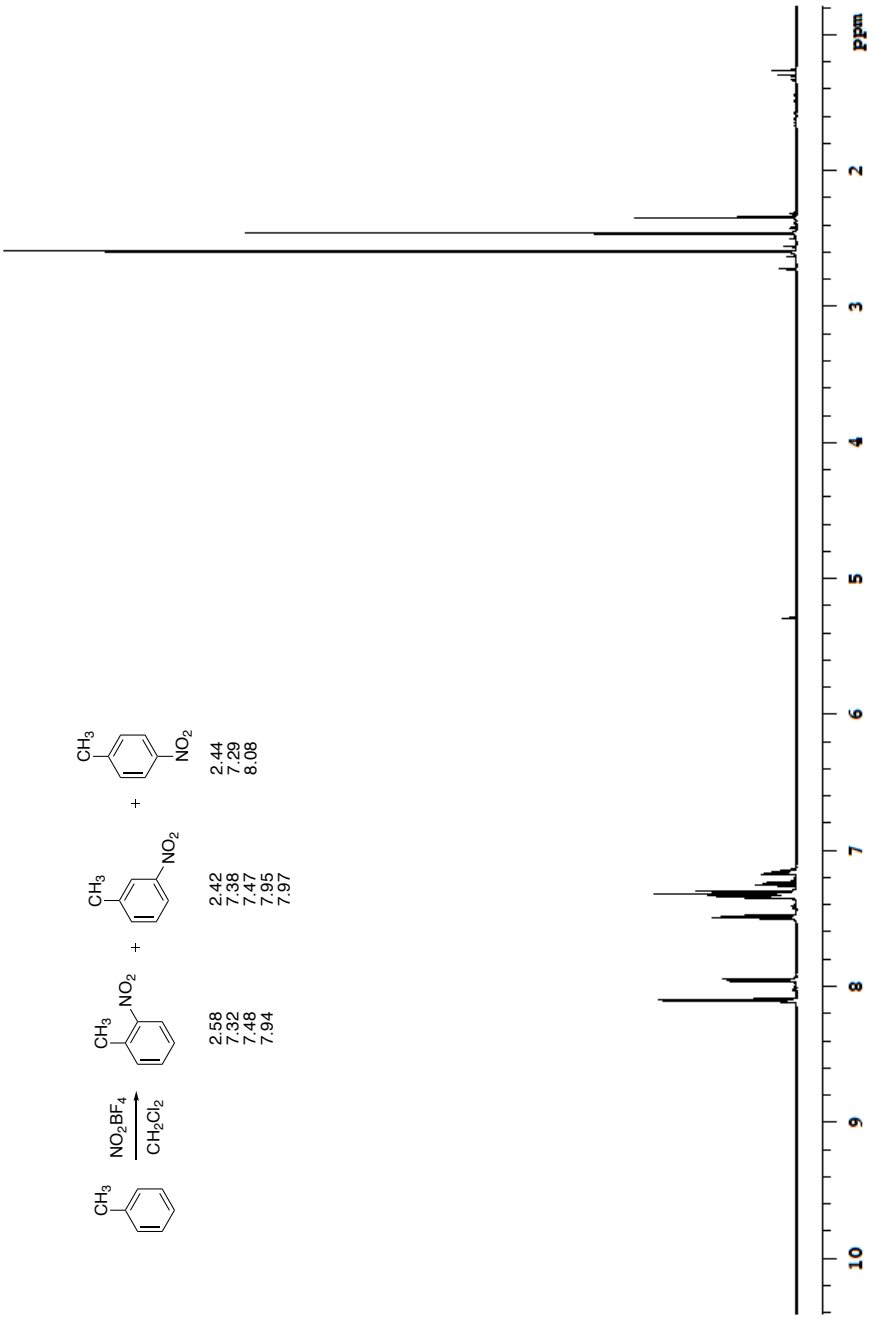
(162) Erkkilä, A.; Pihko, P. M. *J. Org. Chem.* **2006,** *71*, 2538-2541.

(163) Kozmin, S. A.; He, S.; Rawal, V. H. *Organic Synthesis* **2002,** *78*.

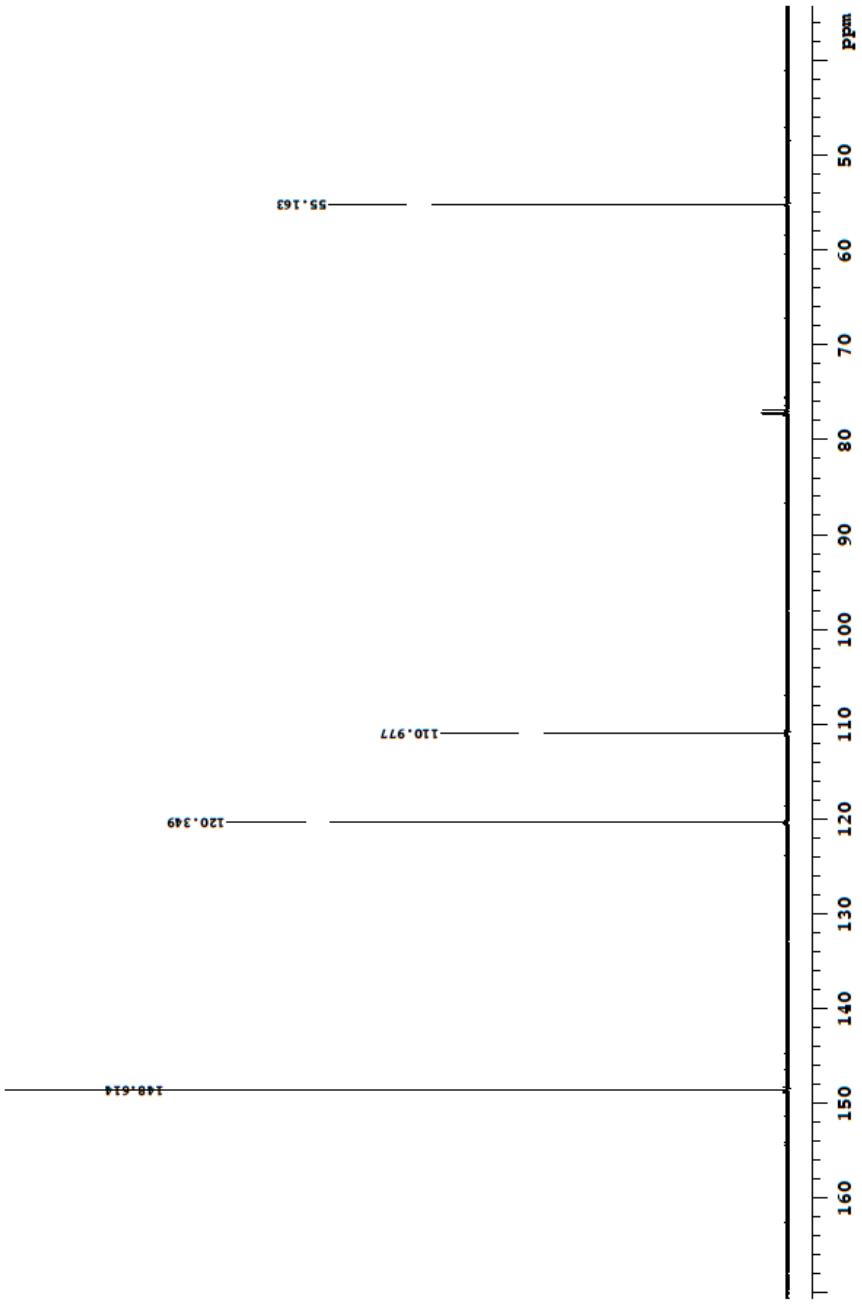
APPENDIX A

NMR DATA

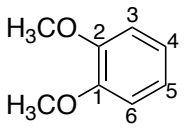
Crude ^{1}H NMR spectrum for the nitration of Toluene in $CDCl_3$



^{13}C NMR Spectrum for the intermolecular KIEs of veratrole in $CDCl_3$



Starting material intermolecular ^{13}C NMR KIEs integrations for the recovered veratrole from the Friedel-Crafts acylation using $AgClO_4$/2,5-di-tert-butylpyridine in CH_2Cl_2



			70%-convertion sample 1			
C1/C2	2000.87	2024.05	2005.31	2031.43	2027.52	2009.20
C4/C5	2020.37	2035.31	2015.27	2041.87	2025.74	2030.10
C3/C6	1985.19	1998.66	1993.72	2003.3	2003.96	1989.08
Methoxy	2000	2000	2000	2000	2000	2000
	Average	*Std. Dev.*	*95% Conf.*	R/R_0	$\Delta(R/R_0)$	
C1/C2	2016.40	12.8	13.5	0.994	0.008	
C4/C5	2028.11	9.8	10.2	1.004	0.007	
C3/C6	1995.65	7.7	8.0	0.998	0.006	
Methoxy	2000.00	0.0	0.0	1.000	0.000	
			Standard 1			
C1/C2	2032.50	2028.23	2015.80	2029.42	2032.17	2037.60
C4/C5	2020.91	2011.46	2009.45	2015.96	2026.91	2030.98
C3/C6	1994.93	2001.16	1987.13	2009.94	1991.07	2009.35
Methoxy	2000	2000	2000	2000	2000	2000
	Average	*Std. Dev.*	*95% Conf.*			
C1/C2	2029.29	7.4	7.7			
C4/C5	2019.28	8.6	9.0			
C3/C6	1998.93	9.5	10.0			
Methoxy	2000.00	0.0	0.0			
			68%-convertion sample 2			
C1/C2	2037.97	2034.46	2051.07	2041.76	2036.00	2043.00
C4/C5	2039.57	2043.56	2047.65	2044.55	2041.08	2044.49
C3/C6	2003.32	2007.83	2013.51	2010.05	2012.11	2006.47
Methoxy	2000	2000	2000	2000	2000	2000
	Average	*Std. Dev.*	*95% Conf.*	R/R_0	$\Delta(R/R_0)$	
C1/C2	2040.71	6.0	6.3	0.997	0.004	
C4/C5	2043.48	2.9	3.0	1.005	0.002	
C3/C6	2008.88	3.8	4.0	0.998	0.003	
Methoxy	2000.00	0.0	0.0	1.000	0.000	
			Standard 2			
C1/C2	2050.27	2042.89	2051.13	2044.56	2052.54	2045.25
C4/C5	2033.33	2030.85	2039.25	2035.58	2032.55	2028.50
C3/C6	2011.65	2006.94	2009.16	2014.22	2015.44	2015.80
Methoxy	2000	2000	2000	2000	2000	2000
	Average	*Std. Dev.*	*95% Conf.*			
C1/C2	2040.71	6.0	6.3			
C4/C5	2043.48	2.9	3.0			
C3/C6	2008.88	3.8	4.0			
Methoxy	2000.00	0.0	0.0			

Starting material intermolecular ^{13}C NMR KIEs integrations for the recovered veratrole from the Friedel-Crafts acylation using $AlBr_3$ in CH_2Cl_2

				82%-conversion sample 1				
C1/C2	1011.39	1015.81	1009.77	1010.49	1011.41	1012.32	1014.68	1007.94
C4/C5	1092.74	1094.79	1090.46	1090.54	1094.59	1091.94	1096.84	1091.19
C3/C6	1085.43	1087.29	1083.38	1081.88	1083.13	1083.85	1085.31	1080.11
Methoxy	1000	1000	1000	1000	1000	1000	1000	1000
C1/C2	1010.25	1013.29	1015.51	1011.67				
C4/C5	1089.99	1091.85	1097.51	1094.9				
C3/C6	1078.55	1086.72	1089.85	1082.71				
Methoxy	1000	1000	1000	1000				
	average	*Std. Dev.*	*95% Conf.*	R/R_0	$\Delta(R/R_0)$			
C1/C2	1012.04	2.4	1.5	0.986	0.002			
C4/C5	1093.11	2.6	1.6	0.997	0.002			
C3/C6	1084.02	3.1	2.0	1.001	0.002			
Methoxy	1000.00	0.0	0.0	1.000	0.000			

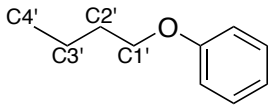
			86%-conversion sample 2			
C1/C2	1020.09	1016.47	1020.08	1016.55	1015.5	1016.87
C4/C5	1099.95	1097.52	1096.88	1097.28	1095.04	1099.62
C3/C6	1088.76	1081.83	1086.53	1085.32	1083.34	1087.9
Methoxy	1000	1000	1000	1000	1000	1000
	Average	*Std. Dev.*	*95% Conf.*	R/R_0	$\Delta(R/R_0)$	
C1/C2	1017.59	2.0	2.1	0.992	0.003	
C4/C5	1097.72	1.8	1.9	1.001	0.003	
C3/C6	1085.61	2.7	2.8	1.002	0.003	
Methoxy	1000.00	0.0	0.0	1.000	0.000	

			Standard			
C1/C2	1025.93	1026.78	1025.41	1023.79	1028.35	1027.64
C4/C5	1094.09	1098.13	1095.26	1095.63	1099.18	1098.2
C3/C6	1081.6	1086.06	1081.85	1082.46	1083.9	1082.79
Methoxy	1000	1000	1000	1000	1000	1000
	Average	*Std. Dev.*	*95% Conf.*			
C1/C2	1026.32	1.6	1.7			
C4/C5	1096.75	2.0	2.1			
C3/C6	1083.11	1.7	1.7			
Methoxy	1000.00	0.0	0.0			

Starting material intermolecular ^{13}C NMR KIEs integrations for the recovered veratrole from the Bromination using Br_2 in acetic acid

			77%-conversion sample 1			
C1/C2	1009.71	1007.76	1009.20	1006.17	1008.62	1007.43
C4/C5	1082.52	1081.40	1079.64	1081.91	1082.78	1079.40
C3/C6	1062.23	1061.53	1060.18	1061.69	1058.82	1060.05
Methoxy	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
	Average	*Std. Dev.*	*95% Conf.*	R/R_0	$\Delta(R/R_0)$	
C1/C2	1008.1	1.3	1.4	0.992	0.002	
C4/C5	1081.3	1.4	1.5	1.005	0.002	
C3/C6	1060.8	1.3	1.3	0.996	0.002	
Methoxy	1000.0	0.0	0.0	1.000	0.000	
			74%-conversion sample 2			
C1/C2	1011.18	1009.35	1011.09	1009.56	1011.99	1010.51
C4/C5	1081.54	1080.40	1081.12	1077.27	1080.48	1079.96
C3/C6	1062.30	1062.25	1061.90	1061.18	1061.32	1062.51
Methoxy	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
	Average	*Std. Dev.*	*95% Conf.*	R/R_0	$\Delta(R/R_0)$	
C1/C2	1010.61	1.0	1.1	0.995	0.002	
C4/C5	1080.13	1.5	1.6	1.004	0.002	
C3/C6	1061.91	0.5	0.6	0.997	0.001	
Methoxy	1000.00	0.0	0.0	1.000	0.000	
			Standard			
C1/C2	1015.49	1014.69	1015.71	1016.93	1017.26	1015.02
C4/C5	1076.47	1075.53	1074.13	1074.95	1077.81	1074.06
C3/C6	1065.42	1065.62	1063.55	1066.61	1066.14	1063.55
Methoxy	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
	Average	*Std. Dev.*	*95% Conf.*			
C1/C2	1015.9	1.0	1.1			
C4/C5	1075.5	1.5	1.5			
C3/C6	1065.1	1.3	1.4			
Methoxy	1000.0	0.0	0.0			

Starting material intermolecular ^{13}C NMR KIEs integrations for the recovered butyl phenyl ether from the Friedel-Crafts acylation using $AlCl_3$ in CH_2Cl_2



				65%-conversion sample 1				
ipso	921.089	919.29	924.598	925.207	930.976	934.134		
meta	2038.97	2025.83	2033.61	2035.21	2027.48	2038.1		
para	997.078	995.511	997.357	1001.17	1000.52	996.744		
ortho	2036.16	2027.17	2030.85	2030.99	2028.14	2030.73		
C1'	980.316	976.745	977.578	972.926	972.824	969.415		
C2'	985.482	979.908	988.421	982.581	987.52	987.431		
C3'	1000	1000	1000	1000	1000	1000		
C4'	999.332	995.973	994.876	994.597	990.704	993.802		
	Average	*Std. Dev.*	*95% Conf.*	*R/R_0*	*$\Delta(R/R_0)$*			
ipso	925.9	5.70	5.98	0.963	0.009			
meta	2033.2	5.45	5.72	1.001	0.003			
para	998.1	2.25	2.37	0.999	0.002			
ortho	2030.7	3.13	3.28	1.001	0.002			
C1'	975.0	3.95	4.15	0.999	0.005			
C2'	985.2	3.34	3.50	0.997	0.004			
C3'	1000.0	0.00	0.00	1.000	0.000			
C4'	994.9	2.82	2.96	0.999	0.003			
				75%-conversion sample 2				
ipso	941.931	947.379	948.73	950.749	949.543	944.426	932.589	940.697
meta	2023.13	2024.71	2028.67	2026.98	2026.89	2025.06	2027.21	2028.19
para	999.875	998.821	1000.75	1003.02	998.55	1001.38	1002.63	1002.67
ortho	2021.34	2023.04	2025.08	2024.47	2022.18	2022.4	2028.68	2028.58
C1'	972.224	974.733	975.888	976.511	973.563	974.005	974.993	972.771
C2'	984.618	985.362	985.621	984.049	983.533	983.449	983.419	985.575
C3'	1000	1000	1000	1000	1000	1000	1000	1000
C4'	994.228	996.762	996.036	995.298	996.123	996.01	993.786	992.778
ipso	946.903	945.459	949.515	941.493				
meta	2027.63	2032.72	2027.45	2029.99				
para	1001.1	1002.03	1000.45	1003.87				
ortho	2029.49	2031.45	2026.97	2031.24				
C1'	976.1	974.901	973.758	976.208				
C2'	984.603	985.038	983.275	988.652				
C3'	1000	1000	1000	1000				
C4'	991.603	992.597	992.602	993.079				
	Average	*Std. Dev.*	*95%*	*R/R_0*	*$\Delta(R/R_0)$*			

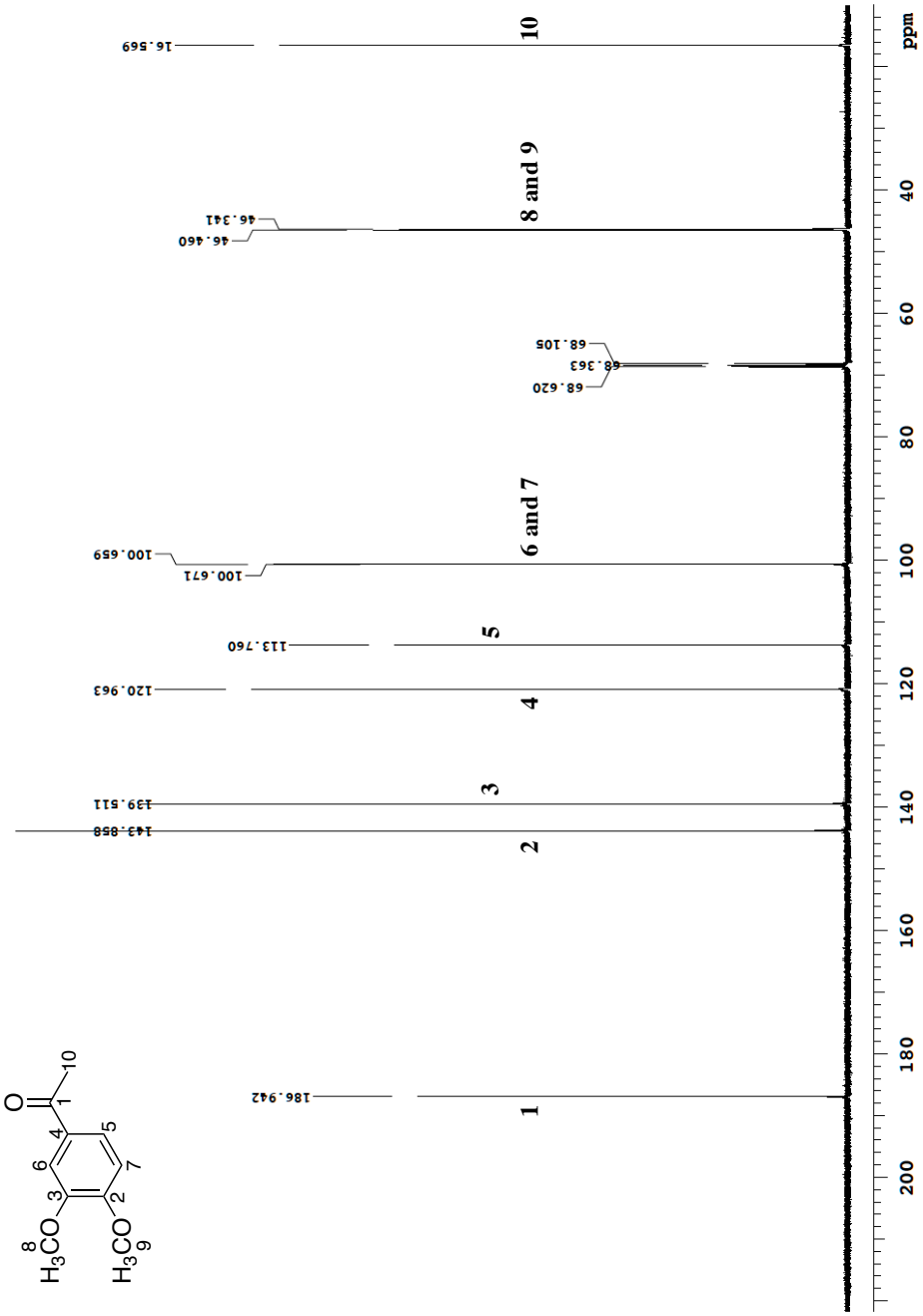
			Conf.			
ipso	945.0	5.15	3.27	0.983	0.008	
meta	2027.4	2.50	1.59	0.998	0.001	
para	1001.3	1.67	1.06	1.002	0.001	
ortho	2026.2	3.63	2.30	0.999	0.002	
C1'	974.6	1.40	0.89	0.999	0.002	
C2'	984.8	1.50	0.95	0.996	0.002	
C3'	1000.0	0.00	0.00	1.000	0.000	
C4'	994.2	1.74	1.11	0.998	0.002	

Standard

ipso	949.301	960.67	961.857	966.541	966.658	965.023
meta	2028.78	2032.07	2029.19	2033.83	2033.25	2033.04
para	998.795	999.027	999.219	1000.17	999.045	998.935
ortho	2025.53	2028.36	2029.39	2032.34	2026.49	2028.47
C1'	972.908	975.23	974.932	977.436	977.303	975.793
C2'	988.117	987.232	989.331	991.413	988.126	987.186
C3'	1000	1000	1000	1000	1000	1000
C4'	996.094	997.884	996.838	993.874	995.705	996.517

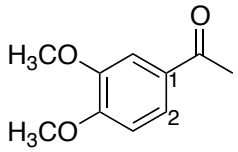
	Average	*Std. Dev.*	*95% Conf.*
ipso	961.7	6.54	6.86
meta	2031.7	2.18	2.28
para	999.2	0.50	0.52
ortho	2028.4	2.38	2.50
C1'	975.6	1.68	1.76
C2'	988.6	1.60	1.68
C3'	1000.0	0.00	0.00
C4'	996.2	1.34	1.41

^{13}C NMR Spectrum for the intramolecular KIEs of 3,4-dimethoxyacetophenone in $CDCl_3$



Peak ratios for individual samples for the 3,4-dimethoxyacetophenone obtained from the Friedel-Crafts acylation of veratrole using $AgClO_4$/2,5-di-tert-butylpyridine in CH_2Cl_2

For each of the 12 spectra, simple peak ratios were calculated for the pair of peaks arising from carbons **1** and **2**. These ratios, their average values, and standard deviations are given in the table below. The results are from two independent samples.



	Sample 1	Sample 2
	1.011	1.011
	1.012	1.005
	1.014	1.011
	1.010	1.014
	1.014	1.008
	1.005	1.010
Average	1.011	1.010
Std. Dev.	0.003	0.003
95% Conf.	0.003	0.003
Adjusted KIE	1.000	0.999

Peak ratios of individual samples for the 3,4-dimethoxyacetophenone obtained from the Friedel-Crafts acylation of veratrole using $AlBr_3$ in CH_2Cl_2 or *o*-$C_6H_4Cl_2$

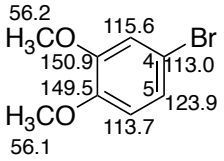
For each of the spectra, simple peak ratios were calculated for the pair of peaks arising from carbons **1** and **2**. These ratios, their average values, and standard deviations are given in the table below. The results are from two independent samples.

CH_2Cl_2 Sample 1	CH_2Cl_2 Sample 2	*o*-$C_6H_4Cl_2$ Sample 1	*o*-$C_6H_4Cl_2$ Sample 2
999.694	995.084	990.432	988.54
1000.52	994.054	992.107	998.079
1001.2	989.489	994.248	991.087
1000.39	1012.31	990.998	991.478
995.101	1010.89	996.261	992.441
999.694	993.704	988.41	992.125
1001.86	1001.77	992.595	997.535
999.845	1001.86	980.941	993.097
1007	1004.48	997.937	987.301
1011.54	1001.41	999.534	1001.54
1007.9	1007.29	994.635	992.018
996.686	1001.16	993.057	994.932
Average	1006.79	1000.17	999.891
1002.0	1007.25	1001.51	989.273
Std. Dev.	995.145	994.951	992.858
4.7	999.58	986.703	990.633
95% Conf.	997.43	991.539	1000.8
3.0	992.552	994.527	997.648
Adjusted KIE	*Average*	*Average*	988.865
0.991	1000.7	993.4	996.57

	Std. Dev. 6.6 *95% Conf.* 3.3 *Adjusted KIE* 0.990	*Std. Dev.* 5.0 *95% Conf.* 2.5 *Adjusted KIE* 0.983	989.58 994.048 1001.03 1001.69 996.774 1001.47 995.834 998.064 998.82 992.589 *Average* 994.9 *Std. Dev.* 4.4 *95% Conf.* 1.6 *Adjusted KIE* 0.984

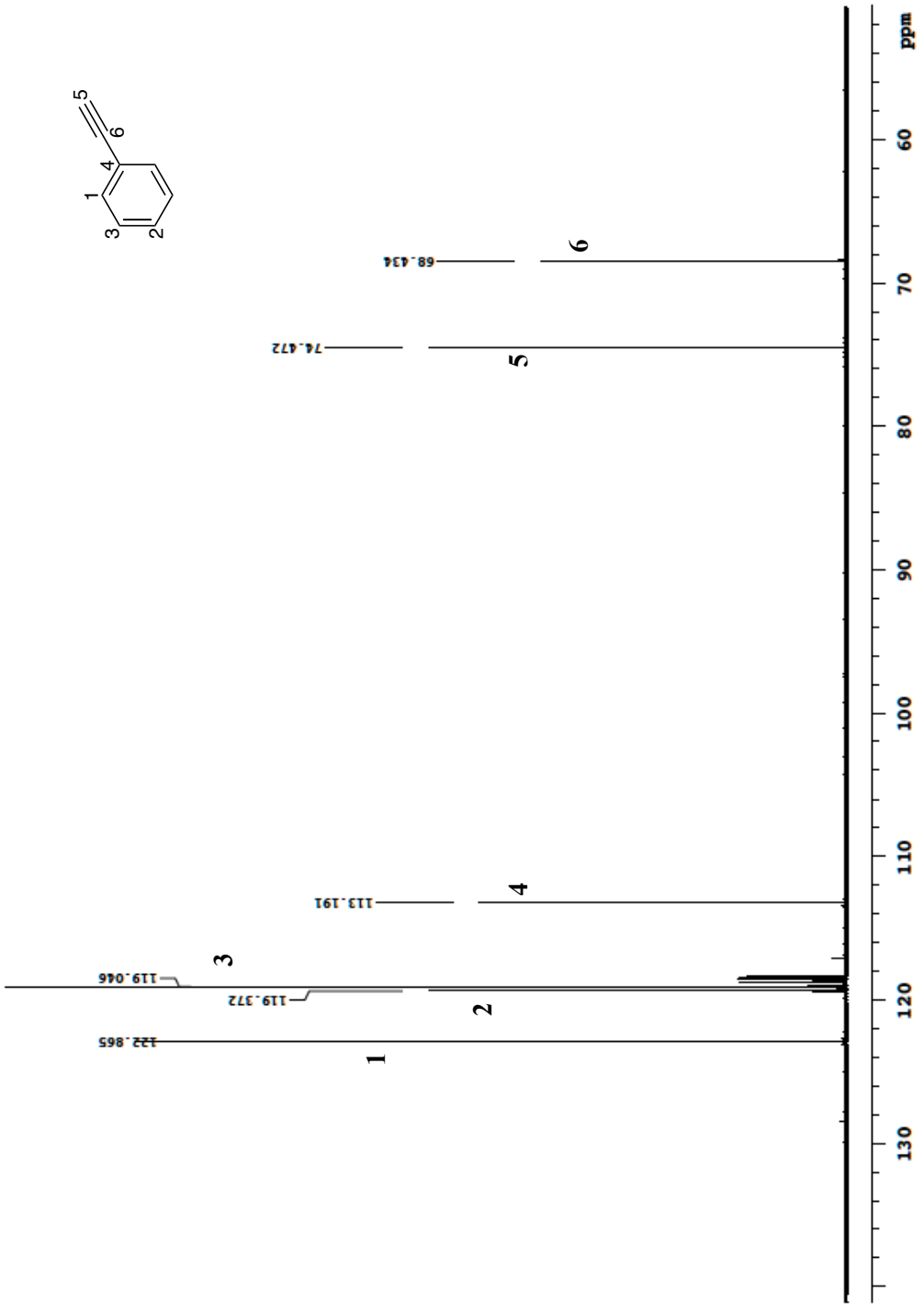
Peak ratios of individual samples for the 4-bromoveratrole obtained from Bromination using Br_2 in acetic acid

The assigned ^{13}C NMR peaks for 4-bromoveratrole in acetone-d_6 are shown below. To determine the ^{13}C isotopic composition at C4 versus C5, the peak at 113.0 for C4 was set to an integration of 1000. The integrations for C5 are then shown in the table below, along with average integrations, standard deviations, and 95% confidence ranges. The KIEs and confidence limits in the main text were then just equal to the averages and 95% confidence limits shown in the table below divided by 1000.

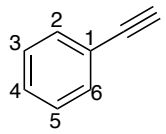


	Sample 1	Sample 2
	1008.31	1015.32
	1014.73	1016.73
	1010.77	1014.47
	1010.26	1012.83
	1010.99	1020.67
	1008.56	1010.96
Average	1010.6	1015.2
Std. Dev.	2.3	3.4
95% Conf.	2.4	3.52

^{13}C NMR Spectrum for the intermolecular KIEs of phenylacetylene in d_6-benzene



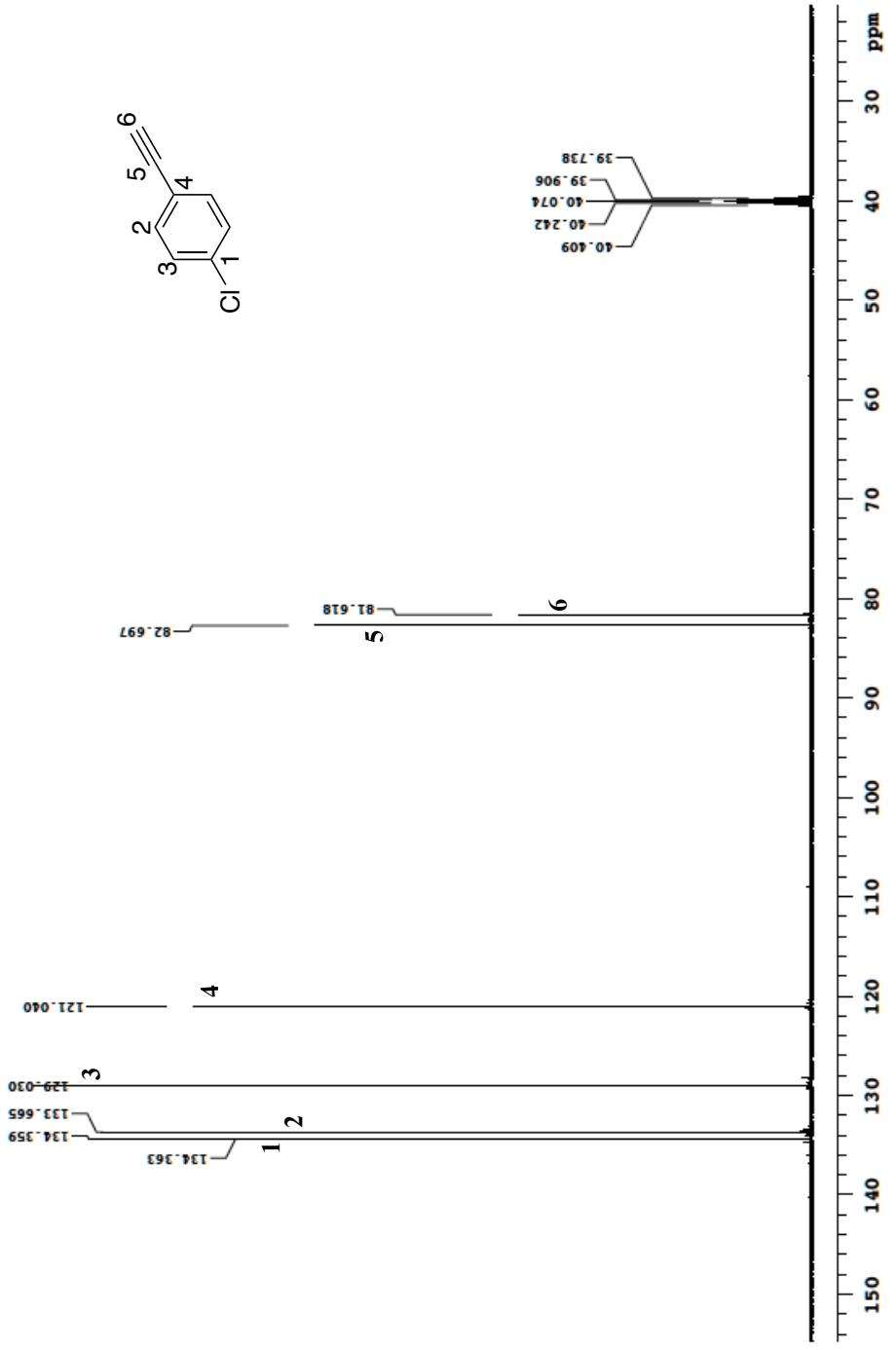
Starting material intermolecular ^{13}C NMR KIEs integrations for the recovered phenylacetylene from the hydroamination reaction



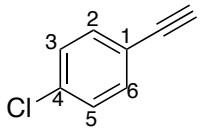
			70%-convertion sample 1			
C1	970.082	968.748	965.349	967.036	966.836	966.731
C2/C6	2000	2000	2000	2000	2000	2000
C3/C5	2029.01	2031.77	2031.34	2034.51	2034.63	2036.76
C4	966.045	967.376	968.323	966.064	965.901	968.02
Internal C	1000.96	1001.9	1008.67	1000	1008.4	1009.79
Terminal C	1009.33	1014.51	1015.75	1010.65	1011.05	1009.14
	Average	*Std. Dev.*	*95% Conf.*	R/R_0	$\Delta(R/R_0)$	
C1	967.46	1.7	1.8	1.005	0.003	
C2/C6	2000	0.0	0.0	1.000	0.000	
C3/C5	2033.00	2.8	2.9	1.003	0.003	
C4	966.95	1.1	1.1	1.006	0.003	
Internal C	1004.95	4.5	4.7	1.017	0.005	
Terminal C	1011.74	2.8	2.9	1.007	0.004	
			Standard 1			
C1	963.40	958.77	965.69	964.28	964.14	960.73
C2/C6	2000	2000	2000	2000	2000	2000
C3/C5	2021.60	2023.99	2023.74	2024.72	2030.86	2031.44
C4	962.91	963.28	961.50	959.98	964.07	956.20
Internal C	986.41	987.05	992.08	988.43	989.04	986.80
Terminal C	1003.39	1003.50	1006.34	1003.46	1003.56	1009.43
	Average	*Std. Dev.*	*95% Conf.*			
C1	962.83	2.6	2.7			
C2/C6	2000	0.0	0.0			
C3/C5	2026.06	4.1	4.3			
C4	961.32	2.9	3.0			
Internal C	988.30	2.1	2.2			
Terminal C	1004.95	2.5	2.6			
			70%-convertion sample 2			
C1	966.565	962.955	963.36	965.456	967.034	964.673
C2/C6	2000	2000	2000	2000	2000	2000
C3/C5	2010.8	2010.76	2007.96	2014.82	2018.48	2010.96
C4	1012.23	1011.96	1008.4	1009.61	1015.64	1014.08
Internal C	1011.96	1002.4	1006.97	1009.73	1012.6	1008.28
Terminal C	1007.77	1001.36	1009.27	1005.77	1011.49	1004.54
	Average	*Std. Dev.*	*95% Conf.*	R/R_0	$\Delta(R/R_0)$	
C1	965.8	2.1	2.2	0.999	0.003	
C2/C6	2000	0.0	0.0	1.000	0.000	
C3/C5	2015.4	4.7	4.9	1.002	0.003	
C4	1013.9	3.0	3.2	1.006	0.004	
Internal C	1009.4	2.8	2.9	1.013	0.004	
Terminal C	1008.5	3.5	3.7	1.007	0.004	
			Standard 2			
C1	968.177	968.359	967.02	966.465	965.167	964.701
C2/C6	2000	2000	2000	2000	2000	2000
C3/C5	2010.76	2013.78	2009.45	2006.58	2012.87	2010.49

C4	1004.78	1005.24	1007.73	1011.16	1005.58	1006.61
Internal C	995.404	1002.74	996.909	992.26	999.076	994.728
Terminal C	1004.33	999.804	1003.36	1002.17	1001.34	997.355
	Average	*Std. Dev.*	*95% Conf.*			
C1	966.4	1.4	1.5			
C2/C6	2000	0.0	0.0			
C3/C5	2011.7	2.5	2.6			
C4	1007.7	2.0	2.1			
Internal C	996.3	2.9	3.0			
Terminal C	1001.3	2.4	2.5			

^{13}C NMR Spectrum for the intermolecular KIEs of *p*-chlorophenylacetylene in d_6-DMSO



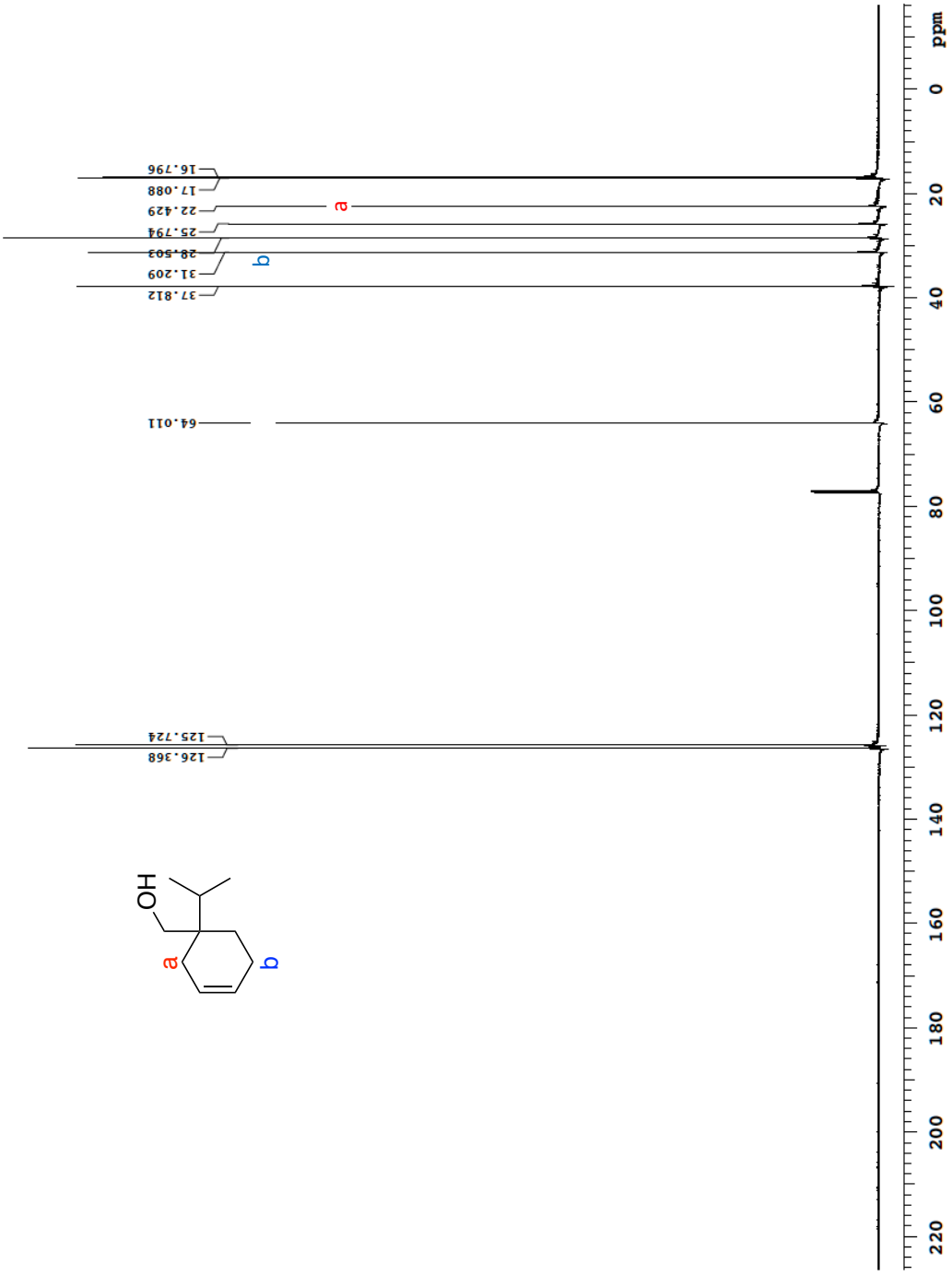
Starting material intermolecular ^{13}C NMR KIEs integrations for the recovered *p*-chlorophenylacetylene from the hydroamination reaction



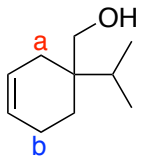
			60%-convertion sample 1			
C1	969.762	965.227	965.97	968.585	968.47	
C2/C6	2000	2000	2000	2000	2000	
C3/C5	2140.751	2113.893	2093.968	2090.189	2087.713	
C4	1031.407	1032.255	1026.05	1027.635	1033.989	
Internal C	1004.31	1010.93	1009.09	1005.51	1005.89	
Terminal C	1043.568	1034.143	1030.454	1035.454	1034.953	
	Average	*Std. Dev.*	*95% Conf.*	R/R_0	$\Delta(R/R_0)$	
C1	967.60	1.9	2.4	0.999	0.004	
C2/C6	2000	0.0	0.0	1.000	0.000	
C3/C5	2105.30	22.3	27.7	0.977	0.013	
C4	1030.27	3.3	4.1	1.004	0.004	
Internal C	1007.15	2.8	3.4	1.023	0.005	
Terminal C	1035.71	4.8	6.0	1.013	0.006	
			Standard 1			
C1	969.227	968.917	973.275	968.882	967.978	962.91
C2/C6	2000	2000	2000	2000	2000	2000
C3/C5	2162.302	2153.631	2153.171	2149.729	2157.35	2148.389
C4	1028.029	1024.394	1025.272	1027.166	1026.576	1024.626
Internal C	985.05	986.66	988.77	983.43	984.10	979.39
Terminal C	1022.38	1023.70	1023.42	1022.07	1019.66	1022.58
	Average	*Std. Dev.*	*95% Conf.*			
C1	968.532	3.3	3.5			
C2/C6	2000	0.0	0.0			
C3/C5	2154.095	5.1	5.4			
C4	1026.011	1.5	1.5			
Internal C	984.567	3.2	3.3			
Terminal C	1022.299	1.4	1.5			
			70%-convertion sample 2			
C1	973.002	970.224	974.477	973.64	975.472	975.424
C2/C6	2000	2000	2000	2000	2000	2000
C3/C5	2001.335	2001.995	2003.732	2001.342	2005.71	2002.512
C4	1024.67	1021.527	1023.176	1019.571	1024.341	1023.293
Internal C	1016.94	1020.75	1021.64	1019.44	1023.35	1021.66
Terminal C	1058.978	1067.301	1063.609	1064.034	1067.551	1063.963
	Average	*Std. Dev.*	*95% Conf.*	R/R_0	$\Delta(R/R_0)$	
C1	973.71	2.0	2.1	1.003	0.003	
C2/C6	2000	0.0	0.0	1.000	0.000	
C3/C5	2002.77	1.7	1.8	0.993	0.002	
C4	1022.76	1.9	2.0	0.990	0.003	
Internal C	1020.63	2.2	2.3	1.032	0.004	
Terminal C	1064.24	3.1	3.3	1.021	0.003	
			Standard 2			
C1	971.398	971.035	971.713	970.123	974.415	968.834
C2/C6	2000	2000	2000	2000	2000	2000
C3/C5	2020.064	2019.217	2013.846	2013.808	2019.163	2010.971

C4	1036.544	1036.066	1030.897	1033.235	1032.868	1031.541
Internal C	990.55	988.82	989.77	986.85	993.73	985.97
Terminal C	1042.42	1041.10	1042.27	1043.51	1044.12	1039.84
	Average	*Std. Dev.*	*95% Conf.*			
C1	971.25	1.9	2.0			
C2/C6	2000	0.0	0.0			
C3/C5	2016.18	3.8	4.0			
C4	1033.53	2.3	2.4			
Internal C	989.28	2.8	2.9			
Terminal C	1042.21	1.6	1.6			

^{13}C NMR Spectrum for the intramolecular KIEs of (1-isopropylcyclohex-3-en-1-yl)methanol in $CDCl_3$



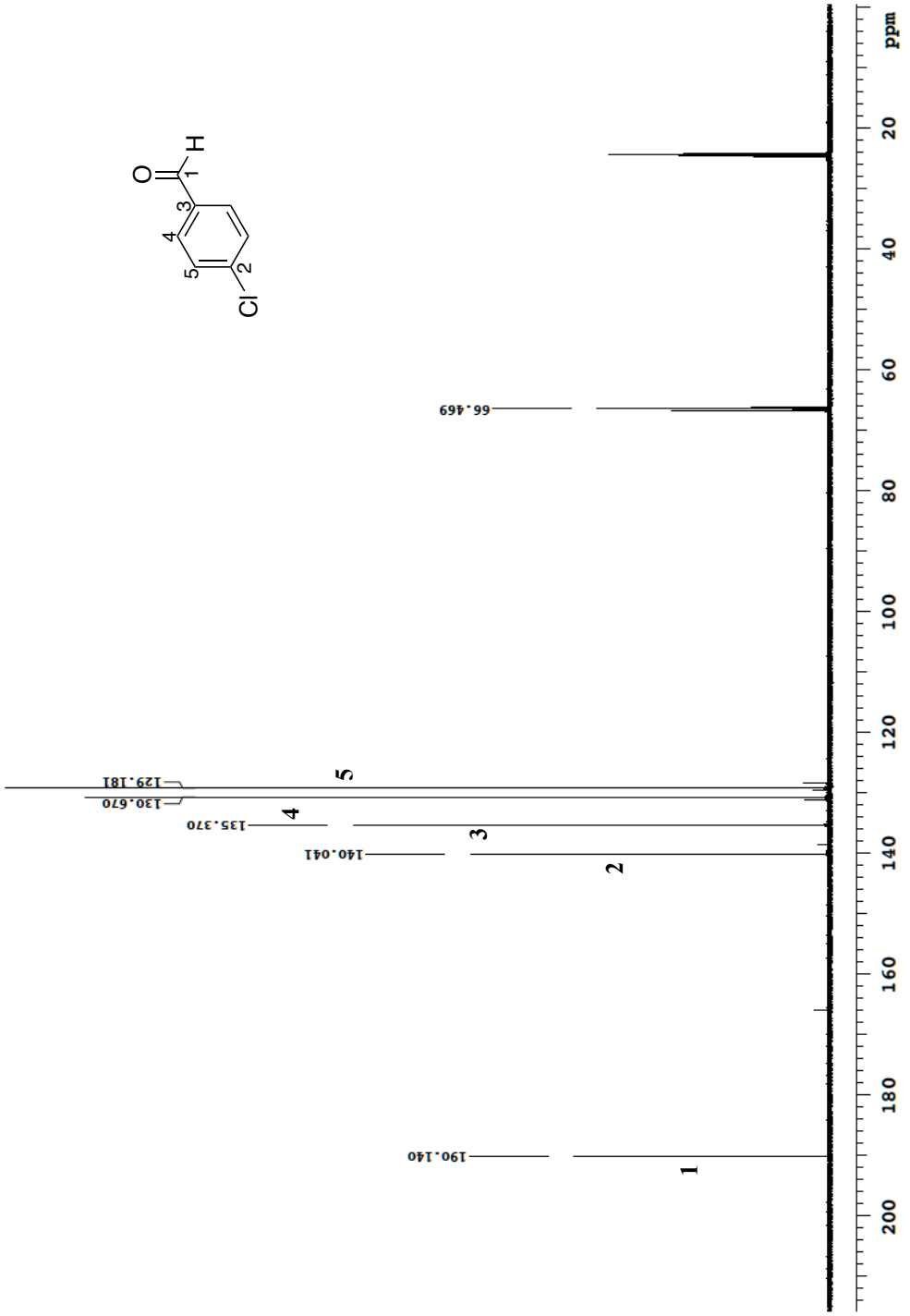
Intramolecular ^{13}C NMR KIE Sample Integration Results for (1-isopropylcyclohex-3-en-1-yl)methanol – From the Lewis acid catalyzed Diels-Alder reaction of 3-methyl-2-methylenebutanal with 1,3-butadiene



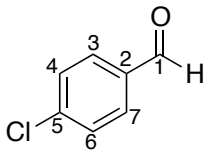
The integrations below are relative to position **b** set as 100.

	Sample 1	**Sample 2**
	1.0277	1.0291
	1.0132	1.0287
	1.0197	1.0302
	1.0221	1.0256
	1.0256	1.0263
	1.0247	1.0266
Average	1.022	1.028
Std. Dev.	0.005	0.002

^{13}C NMR Spectrum for the intermolecular KIEs of *p*-chlorobenzaldehyde in d_8-THF



Starting material intermolecular ^{13}C NMR KIEs integrations for the recovered *p*-chlorobenzaldehyde from the Diels-Alder cycloaddition with (*E*)-1-dimethylamino-3-tert-butyldimethylsiloxy-1,3-butadiene



			70%-convertion sample 1			
C1	985.415	978.919	978.959	976.553	983.128	980.502
C2	988.486	986.684	987.862	989.812	986.161	989.197
C3/C7	1995.83	1991.91	1996.77	1990.70	1991.33	1996.45
C4/C6	2000.00	2000.00	2000.00	2000.00	2000.00	2000.00
C5	987.566	985.382	986.470	984.315	982.834	984.416
	Average	*Std. Dev.*	*95% Conf.*	R/R_0	$\Delta(R/R_0)$	
C1	980.579	3.2	3.4	1.003	0.005	
C2	988.034	1.4	1.5	0.995	0.003	
C3/C7	1993.832	2.8	2.9	0.998	0.002	
C4/C6	2000.000	0.0	0.0	1.000	0.000	
C5	985.164	1.7	1.8	0.995	0.004	
			Standard 1			
C1	980.071	971.686	976.535	981.702	975.526	980.79
C2	990.717	990.464	992.258	995.506	994.352	993.253
C3/C7	1998.3	1993.27	1997.41	2003.25	2001.22	1998.98
C4/C6	2000.00	2000.00	2000.00	2000.00	2000.00	2000.00
C5	987.251	986.493	991.196	992.635	993.363	988.695
	Average	*Std. Dev.*	*95% Conf.*			
C1	977.718	3.8	4.0			
C2	992.758	2.0	2.1			
C3/C7	1998.738	3.4	3.6			
C4/C6	2000.000	0.0	0.0			
C5	989.939	2.9	3.0			
			70%-convertion sample 2			
C1	974.907	979.891	982.237	975.383	982.347	976.397
C2	999.96	997.055	998.325	1003.15	999.703	999.969
C3/C7	1998.72	1997.85	1996.6	1994.03	1995.01	1997.8
C4/C6	2000.00	2000.00	2000.00	2000.00	2000.00	2000.00
C5	997.216	1000.44	995.784	1002.46	999.631	996.342
	Average	*Std. Dev.*	*95% Conf.*	R/R_0	$\Delta(R/R_0)$	
C1	978.527	3.4	3.6	1.005	0.004	
C2	999.694	2.0	2.1	0.998	0.002	
C3/C7	1996.668	1.8	1.9	1.001	0.001	
C4/C6	2000.000	0.0	0.0	1.000	0.000	
C5	998.646	2.6	2.7	1.002	0.003	
			Standard 2			
C1	976.034	971.128	975.134	973.667	974.158	972.031
C2	999.96	997.055	998.325	1003.15	999.703	999.969
C3/C7	1998.72	1997.85	1996.6	1994.03	1995.01	1997.8
C4/C6	2000.00	2000.00	2000.00	2000.00	2000.00	2000.00
C5	997.216	1000.44	995.784	1002.46	999.631	996.342
	Average	*Std. Dev.*	*95% Conf.*			
C1	978.527	3.4	3.6			

C2	999.694	2.0	2.1
C3/C7	1996.668	1.8	1.9
C4/C6	2000.000	0.0	0.0
C5	998.646	2.6	2.7

APPENDIX B

STRUCTURES, ENERGIES AND COMPUTATIONAL PROGRAMS

Calculated Structures for the Nitration of Toluene

Toluene M062X/6-311G*/PCM(CH_2Cl_2)
M062X/6-311G*
E(RM062X) = -271.495957959

Zero-point correction= 0.128768 (Hartree/Particle)
Thermal correction to Energy= 0.134919
Thermal correction to Enthalpy= 0.135863
Thermal correction to Gibbs Free Energy= 0.098498
Sum of electronic and ZPE= -271.367190
Sum of electronic and thermal Energies= -271.361039
Sum of electronic and thermal Enthalpies= -271.360095
Sum of electronic and thermal Free Energies= -271.397460

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	84.663	23.067	78.640

C,0,0.9255051816,1.9370543762,0.0057654806
C,0,1.0098007575,1.2375724004,1.2064981383
C,0,1.1869602,-0.1419972957,1.199941624
C,0,1.284754455,-0.8481474363,-0.0010834637
C,0,1.1963030969,-0.1355138276,-1.1978033889
C,0,1.0190097515,1.2451366148,-1.1975078481
C,0,1.5061423469,-2.3389391059,-0.0002698899
H,0,0.7844816855,3.0119095013,0.0085174978
H,0,0.9338148302,1.767208922,2.1498296396
H,0,1.2484042735,-0.6817083439,2.1403208093
H,0,1.2648270094,-0.6689711516,-2.1410921768
H,0,0.9503454097,1.7799882021,-2.1384493338
H,0,1.1685149351,-2.7912053875,-0.933916141
H,0,0.9746972721,-2.8180741361,0.8238800437
H,0,2.5680077949,-2.5733583322,0.115225009

NO_2^+ M062X/6-311G*/PCM(CH_2Cl_2)
M062X/6-311G*
E(RM062X) = -204.788876622

Zero-point correction= 0.012555 (Hartree/Particle)
Thermal correction to Energy= 0.015140
Thermal correction to Enthalpy= 0.016085

Thermal correction to Gibbs Free Energy= -0.008096
Sum of electronic and ZPE= -204.776322
Sum of electronic and thermal Energies= -204.773736
Sum of electronic and thermal Enthalpies= -204.772792
Sum of electronic and thermal Free Energies= -204.796972

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 9.501 6.672 50.892

N,0,0.,0.,0.
O,0,0.,0.,1.1050096647
O,0,0.,0.,-1.1050096647

TSs for Toluene + NO_2^+ M062X/6-311G*/PCM(CH_2Cl_2)
TS Toluene + NO_2^+ ipso 190031
M062X/6-311G*
E(RM062X) = -476.296115891

Zero-point correction= 0.141325 (Hartree/Particle)
Thermal correction to Energy= 0.150604
Thermal correction to Enthalpy= 0.151548
Thermal correction to Gibbs Free Energy= 0.106085
Sum of electronic and ZPE= -476.154791
Sum of electronic and thermal Energies= -476.145512
Sum of electronic and thermal Enthalpies= -476.144567
Sum of electronic and thermal Free Energies= -476.190031

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.506 33.264 95.686

C,0,2.1672683791,0.2486907575,-0.0004712612
C,0,1.5625348931,-0.0974844662,1.2081640532
C,0,0.3528173158,-0.7780810616,1.2088488719
C,0,-0.2726812838,-1.1334771936,-0.0002270444
C,0,0.3518313009,-0.7767183139,-1.2094310257
C,0,1.5615584322,-0.0961373784,-1.2089937919
C,0,-1.5482229909,-1.92620715,-0.0002035311
H,0,3.1109815205,0.7810412512,-0.0005534484
H,0,2.0368034317,0.1634132127,2.1466030878
H,0,-0.1103170428,-1.0632187373,2.1477619935
H,0,-0.1121037368,-1.0607846902,-2.1482740695
H,0,2.0350421274,0.16583767,-2.1475302639
H,0,-2.4330309543,-1.279601995,-0.0004969304
H,0,-1.6138415968,-2.5570191297,0.886310191
H,0,-1.6135964559,-2.5573480016,-0.8865091068
N,0,-1.1032373006,1.4195320168,0.0007037226
O,0,-0.1516379665,2.0013528584,0.0011227659
O,0,-2.1768570722,1.102142351,0.0004667874

TS Toluene + NO_2^+ ortho 187860
M062X/6-311G*
E(RM062X) = -476.294517695

Zero-point correction= 0.141530 (Hartree/Particle)
Thermal correction to Energy= 0.150793
Thermal correction to Enthalpy= 0.151737
Thermal correction to Gibbs Free Energy= 0.106658
Sum of electronic and ZPE= -476.152987
Sum of electronic and thermal Energies= -476.143725
Sum of electronic and thermal Enthalpies= -476.142781
Sum of electronic and thermal Free Energies= -476.187860

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.624 33.285 94.876

C,0,-0.5370453891,1.6439196992,-0.3417689813
C,0,0.3000637444,1.62370211,0.770636242
C,0,1.3745771267,0.7145044368,0.8312402415
C,0,1.6384611575,-0.1693810902,-0.2244298334
C,0,0.7695380963,-0.1536089411,-1.3108920962
C,0,-0.3082690004,0.7394096259,-1.3699189916
C,0,2.7927172121,-1.1306323004,-0.150534918
H,0,-1.3587472313,2.3467319397,-0.3966609169
H,0,0.1439539419,2.3202021322,1.5873903479
H,0,2.0347425662,0.7297203351,1.6934500313
H,0,0.9323034965,-0.842482785,-2.1330428887
H,0,-0.9624323514,0.726329728,-2.2337266311
H,0,3.6561540251,-0.6707058127,0.3312374874
H,0,3.0888765539,-1.4657179193,-1.1441972936
H,0,2.5196327958,-2.0144126616,0.432365723
N,0,-0.6052259966,-0.5593893368,1.8464850176
O,0,-1.027666461,-1.049203666,0.932046291
O,0,-0.4143452866,-0.3235974938,2.9288431692

TS Toluene + NO_2^+ ortho 188821
M062X/6-311G*
E(RM062X) = -476.294566581

Zero-point correction= 0.141190 (Hartree/Particle)
Thermal correction to Energy= 0.150618
Thermal correction to Enthalpy= 0.151562

Thermal correction to Gibbs Free Energy= 0.105746
Sum of electronic and ZPE= -476.153376
Sum of electronic and thermal Energies= -476.143948
Sum of electronic and thermal Enthalpies= -476.143004
Sum of electronic and thermal Free Energies= -476.188821

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.514 33.406 96.429

C,0,1.1834182488,-1.8213603392,-0.0074468132
C,0,0.9036265049,-1.102631014,-1.1637612621
C,0,0.8259477107,0.2938919668,-1.1352153998
C,0,1.0259422288,1.0087213506,0.0438879169
C,0,1.3547508915,0.2826590341,1.194334319
C,0,1.4244269157,-1.1267622855,1.173141158
C,0,0.9117097384,2.5081850653,0.0656010201
H,0,1.2264246262,-2.902957644,-0.0262113719
H,0,0.7369076795,-1.625649349,-2.0980560501
H,0,0.5995344072,0.832506658,-2.0497745405
H,0,1.5201075769,0.8068040156,2.1307018113
H,0,1.6469561262,-1.6628552483,2.0894211457
H,0,1.5979451274,2.9618720438,-0.6523402558
H,0,1.1313160887,2.9108719742,1.0539170941
H,0,-0.098847885,2.8158046412,-0.2101700001
N,0,3.7803704251,-0.2366731594,0.5802599905
O,0,3.715183174,-0.2623974668,-0.5381135981
O,0,4.2269824149,-0.1963352435,1.6116498359

TS Toluene + NO_2^+ para 189331
M062X/6-311G*
E(RM062X) = -476.295678690

Zero-point correction= 0.141612 (Hartree/Particle)
Thermal correction to Energy= 0.150949
Thermal correction to Enthalpy= 0.151893
Thermal correction to Gibbs Free Energy= 0.106347
Sum of electronic and ZPE= -476.154067
Sum of electronic and thermal Energies= -476.144729
Sum of electronic and thermal Enthalpies= -476.143785
Sum of electronic and thermal Free Energies= -476.189331

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.722 33.253 95.860

C,0,-0.5435533055,1.6133674884,-0.3083296762
C,0,0.3318768929,1.6372581043,0.7809606653
C,0,1.3936532979,0.7494258262,0.8254657678
C,0,1.6309136573,-0.1586602508,-0.2229857734
C,0,0.777579219,-0.1452924296,-1.3266777776
C,0,-0.3073665484,0.724622953,-1.3710041813
C,0,2.7751687066,-1.1264478982,-0.1321259101
H,0,-1.376263163,2.3065628837,-0.354950136
H,0,0.1703229618,2.3373176015,1.5918387775

H,0,2.062570149,0.7529677609,1.6798062069
H,0,0.9552977155,-0.8253658824,-2.1524845045
H,0,-0.965379832,0.7289997335,-2.2329649359
H,0,3.6727159558,-0.6350459515,0.2466695322
H,0,3.0017548639,-1.5700743604,-1.1009643816
H,0,2.5301109804,-1.9359216135,0.5613325559
N,0,-1.8065947214,-0.5303172071,0.4876200744
O,0,-0.9554220161,-1.081052024,0.956302857
O,0,-2.8312568138,-0.2131517339,0.1622928397

TS Toluene + NO_2^+ para 189465
M062X/6-311G*
E(RM062X) = -476.295695036

Zero-point correction= 0.141612 (Hartree/Particle)
Thermal correction to Energy= 0.150957
Thermal correction to Enthalpy= 0.151901
Thermal correction to Gibbs Free Energy= 0.106230
Sum of electronic and ZPE= -476.154083
Sum of electronic and thermal Energies= -476.144738
Sum of electronic and thermal Enthalpies= -476.143794
Sum of electronic and thermal Free Energies= -476.189465

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.727 33.262 96.123

C,0,1.2371176234,-1.8033976043,-0.0727628045
C,0,1.0643492992,-1.0837595813,-1.2588237738
C,0,0.9829704918,0.2975163754,-1.2154069276
C,0,1.0367001984,0.9948047667,0.0061344534
C,0,1.1685482115,0.2660518842,1.1877953072
C,0,1.2766097832,-1.1213122454,1.1546614612
C,0,0.9480607965,2.4937237333,0.0128894923
H,0,1.2989703182,-2.8859238401,-0.0951762409
H,0,1.0105049196,-1.605076008,-2.2070036433
H,0,0.8693324356,0.8596753922,-2.1366152781
H,0,1.1964176281,0.7844498648,2.1398327963
H,0,1.3772231459,-1.6802446042,2.0784899098
H,0,0.0432919158,2.8261028619,-0.500587567
H,0,1.7989605335,2.9301513584,-0.5161251439
H,0,0.9350811516,2.8899775451,1.0273550526
N,0,3.7789779476,-1.234438154,0.152308798
O,0,3.771553092,-0.1998956799,-0.2680767254
O,0,4.104723508,-2.2297850648,0.5512668336

Product Structures for Toluene + NO_2^+ M062X/6-311G*/PCM(CH_2Cl_2)
ipso Product 206704
M062X/6-311G*
E(RM062X) = -476.316372222

Zero-point correction= 0.143680 (Hartree/Particle)
Thermal correction to Energy= 0.152373
Thermal correction to Enthalpy= 0.153317
Thermal correction to Gibbs Free Energy= 0.109668
Sum of electronic and ZPE= -476.172692
Sum of electronic and thermal Energies= -476.163999
Sum of electronic and thermal Enthalpies= -476.163055
Sum of electronic and thermal Free Energies= -476.206704

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.615 32.893 91.867

C,0,2.506597,0.004363,-0.35746
C,0,1.821609,1.235953,-0.366006
C,0,0.47896,1.246062,-0.150502
C,0,-0.222044,0.01277,0.247585
C,0,0.522533,-1.248143,0.090584
C,0,1.864563,-1.229623,-0.126688
C,0,-0.507674,0.15364,1.802645
H,0,3.571186,0.00263,-0.565688
H,0,2.354653,2.150549,-0.586194
H,0,-0.104587,2.158665,-0.19314
H,0,-0.019763,-2.174855,0.236525
H,0,2.43285,-2.148781,-0.161972
H,0,-1.080621,1.065581,1.957271
H,0,0.433726,0.199061,2.345977
H,0,-1.083665,-0.714579,2.118651
N,0,-1.621983,-0.053778,-0.384001
O,0,-2.212164,0.990342,-0.471944
O,0,-2.029981,-1.141836,-0.691102

meta Product 209211
M062X/6-311G*
E(RM062X) = -476.317016634

Zero-point correction= 0.142484 (Hartree/Particle)
Thermal correction to Energy= 0.151453
Thermal correction to Enthalpy= 0.152398
Thermal correction to Gibbs Free Energy= 0.107805
Sum of electronic and ZPE= -476.174532
Sum of electronic and thermal Energies= -476.165563
Sum of electronic and thermal Enthalpies= -476.164619
Sum of electronic and thermal Free Energies= -476.209211

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.038 33.084 93.852

C,0,0.6875660452,-0.9364256012,-0.9367337752
C,0,1.3651837913,-2.0179307942,-0.4642351184
C,0,1.0332425181,-2.5417915931,0.7991123413
C,0,0.0131984715,-2.0266758448,1.6373168672
C,0,-0.6810987093,-0.9433043686,1.1807802261
C,0,-0.47358629,-0.4478800693,-0.1859691639
C,0,-0.2312838456,-2.6380690569,2.9859509581
H,0,0.9255971391,-0.4616764054,-1.880511529
H,0,2.1837123664,-2.4467666137,-1.0260582439
H,0,1.616551419,-3.3806323103,1.1688235704
H,0,-1.4504463492,-0.4634519897,1.7750905966
H,0,-1.3267598862,-0.9068428154,-0.7440467929
H,0,-0.9925709358,-2.0857612344,3.5334029514
H,0,0.6876332382,-2.6431063251,3.5740878912
H,0,-0.5645612667,-3.6712126057,2.8742500394
N,0,-0.7395716363,1.0490398443,-0.3573132393
O,0,-1.4159341394,1.572198211,0.4857827191
O,0,-0.2836009304,1.5618415724,-1.3430902979

ortho Product 21298
M062X/6-311G*
E(RM062X) = -476.321390301

Zero-point correction= 0.142993 (Hartree/Particle)
Thermal correction to Energy= 0.151863
Thermal correction to Enthalpy= 0.152808
Thermal correction to Gibbs Free Energy= 0.108406
Sum of electronic and ZPE= -476.178398
Sum of electronic and thermal Energies= -476.169527
Sum of electronic and thermal Enthalpies= -476.168583
Sum of electronic and thermal Free Energies= -476.212984

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.296 32.771 93.451

C,0,0.650428293,-1.1992474621,-1.795157402
C,0,1.5325085093,-2.1117890349,-1.1643259315
C,0,1.7226048612,-2.1671676253,0.2185232456
C,0,1.0450435924,-1.3166595151,1.0610808633
C,0,-0.0227372038,-0.4747224968,0.4450134691
C,0,-0.0549840997,-0.3402510706,-1.0252190145
C,0,1.2929319815,-1.2931890461,2.5216796779
H,0,0.5797483773,-1.1722367306,-2.8736400517
H,0,2.1145662045,-2.7813270832,-1.7887074913
H,0,2.4506172289,-2.8553839476,0.6287653644
H,0,-0.9433448888,-1.0532509394,0.6763450913
H,0,-0.7193435995,0.4041219837,-1.4474785467
H,0,1.654117331,-0.3045206563,2.8226938318
H,0,2.0326571462,-2.0413783639,2.7943975211

H,0,0.3688602558,-1.4622969597,3.0784768328
N,0,-0.2266439519,0.8506886157,1.1539514622
O,0,0.0610957192,1.8443606703,0.5390414736
O,0,-0.6520597569,0.7957206618,2.2797696049

para Product 218203
M062X/6-311G*
E(RM062X) = -476.325950643

Zero-point correction= 0.142396 (Hartree/Particle)
Thermal correction to Energy= 0.151304
Thermal correction to Enthalpy= 0.152248
Thermal correction to Gibbs Free Energy= 0.107747
Sum of electronic and ZPE= -476.183555
Sum of electronic and thermal Energies= -476.174647
Sum of electronic and thermal Enthalpies= -476.173702
Sum of electronic and thermal Free Energies= -476.218203

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.945 32.968 93.660

C,0,0.7360771244,-0.0002709661,0.469881242
C,0,0.0164015985,1.2589692412,0.2082599022
C,0,-1.321469905,1.2404089282,0.0097718584
C,0,-2.0203607344,0.0034402296,-0.0896358402
C,0,-1.3250793597,-1.2348623369,0.0071751287
C,0,0.0134388178,-1.2567114434,0.2043274759
C,0,-3.4813133516,0.0101271303,-0.2967286415
H,0,0.8821685472,-0.002735125,1.5728435287
H,0,0.5800106178,2.182728102,0.2494004641
H,0,-1.8684945708,2.1661756168,-0.1173216544
H,0,-1.8737530075,-2.1590676372,-0.1224074629
H,0,0.5751813784,-2.1818354006,0.2409845196
H,0,-3.8064567059,0.8783877945,-0.869231685
H,0,-3.9407247489,0.0955409055,0.6994154673
H,0,-3.8415112524,-0.9139319814,-0.7445300402
N,0,2.1747266763,-0.0015604569,-0.0497654389
O,0,2.685314064,-1.0774286123,-0.2104573187
O,0,2.6876478118,1.0733580117,-0.2091555052

Pi Complexes for Toluene + NO_2^+ M062X/6-311G*/PCM(CH_2Cl_2)
ipso N-Pi complex 191410
M062X/6-311G*
E(RM062X) = -476.296104866

Zero-point correction= 0.141850 (Hartree/Particle)
Thermal correction to Energy= 0.151978
Thermal correction to Enthalpy= 0.152922
Thermal correction to Gibbs Free Energy= 0.104695

Sum of electronic and ZPE= -476.154255
Sum of electronic and thermal Energies= -476.144127
Sum of electronic and thermal Enthalpies= -476.143183
Sum of electronic and thermal Free Energies= -476.191410

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.367 35.073 101.502

C,0,2.1495738018,-0.342989473,0.0010760284
C,0,1.5634500941,0.0367593582,-1.205514675
C,0,0.3929824921,0.7871233338,-1.2055983562
C,0,-0.2085796583,1.1803138549,0.0003221646
C,0,0.3912230097,0.7854893348,1.206645806
C,0,1.5616892812,0.0351389838,1.2073112094
C,0,-1.4461688013,2.0353549772,0.0001138875
H,0,3.0626734946,-0.9263808186,0.0013425784
H,0,2.020695139,-0.2498637761,-2.1451980265
H,0,-0.0513773844,1.0974455012,-2.1458353572
H,0,-0.0546069085,1.0945482965,2.1466102715
H,0,2.0174540454,-0.252898714,2.147284871
H,0,-2.3622220767,1.4342907718,0.0019340372
H,0,-1.4814434913,2.668908275,-0.8863188681
H,0,-1.4798039232,2.6715282648,0.884751737
N,0,-1.1925076611,-1.4507996971,-0.0017056564
O,0,-0.243491035,-2.0266656288,-0.0011828152
O,0,-2.2254434184,-1.0339338445,-0.0021618366

ipso O-Pi complex 186028
M062X/6-311G*
E(RM062X) = -476.291663427

Zero-point correction= 0.142539 (Hartree/Particle)
Thermal correction to Energy= 0.152465
Thermal correction to Enthalpy= 0.153409
Thermal correction to Gibbs Free Energy= 0.105636
Sum of electronic and ZPE= -476.149124
Sum of electronic and thermal Energies= -476.139199
Sum of electronic and thermal Enthalpies= -476.138255
Sum of electronic and thermal Free Energies= -476.186028

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.673 34.509 100.547

C,0,-1.48808,-1.699732,0.000349
C,0,-1.356044,-1.010326,1.202963
C,0,-1.089886,0.356829,1.200512
C,0,-0.948409,1.060087,0.00026
C,0,-1.09165,0.357085,-1.199934

C,0,-1.357813,-1.010066,-1.202307
C,0,-0.607395,2.527007,0.000153
H,0,-1.700661,-2.762387,0.000391
H,0,-1.467367,-1.534712,2.145302
H,0,-0.9948,0.887147,2.143069
H,0,-0.997926,0.887629,-2.142499
H,0,-1.470543,-1.534213,-2.144611
H,0,-1.003142,3.02686,0.884942
H,0,-1.003616,3.02686,-0.884413
H,0,0.477968,2.668915,-0.000126
N,0,2.426069,-0.358906,-0.000576
O,0,1.365184,-0.67207,-0.001319
O,0,3.486474,-0.032813,0.000069

meta N-Pi complex 189935
M062X/6-311G*
E(RM062X) = -476.295961987

Zero-point correction= 0.142018 (Hartree/Particle)
Thermal correction to Energy= 0.151977
Thermal correction to Enthalpy= 0.152922
Thermal correction to Gibbs Free Energy= 0.106027
Sum of electronic and ZPE= -476.153944
Sum of electronic and thermal Energies= -476.143985
Sum of electronic and thermal Enthalpies= -476.143040
Sum of electronic and thermal Free Energies= -476.189935

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.367 34.945 98.698

C,0,-0.566614,1.648636,-0.150145
C,0,0.231864,1.514868,0.98521
C,0,1.2888,0.612055,0.988483
C,0,1.581413,-0.167274,-0.139716
C,0,0.785221,-0.0152,-1.274862
C,0,-0.283342,0.881319,-1.283076
C,0,2.725979,-1.14336,-0.113405
H,0,-1.387225,2.357201,-0.16302
H,0,0.027435,2.11257,1.865867
H,0,1.903554,0.5082,1.877152
H,0,1.002174,-0.599212,-2.163031
H,0,-0.886114,0.993253,-2.178069
H,0,2.856685,-1.628261,-1.080674
H,0,2.558038,-1.91948,0.637275
H,0,3.658998,-0.63851,0.144967
N,0,-1.904649,-0.889763,0.289032
O,0,-1.051926,-1.255747,0.893449
O,0,-2.82069,-0.612213,-0.273277

meta N-Pi complex 190153
M062X/6-311G*
E(RM062X) = -476.295477416

Zero-point correction= 0.141922 (Hartree/Particle)
Thermal correction to Energy= 0.151957
Thermal correction to Enthalpy= 0.152901
Thermal correction to Gibbs Free Energy= 0.105325
Sum of electronic and ZPE= -476.153555
Sum of electronic and thermal Energies= -476.143521
Sum of electronic and thermal Enthalpies= -476.142577
Sum of electronic and thermal Free Energies= -476.190153

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.354 34.932 100.132

C,0,0.354336,-1.781366,-0.365589
C,0,-0.528191,-1.723467,0.710543
C,0,-1.432964,-0.670576,0.816742
C,0,-1.484007,0.342912,-0.147074
C,0,-0.59152,0.279199,-1.218414
C,0,0.320365,-0.773966,-1.329731
C,0,-2.495812,1.452365,-0.045294
H,0,1.054198,-2.603415,-0.458484
H,0,-0.512272,-2.498297,1.468294
H,0,-2.115987,-0.634645,1.659596
H,0,-0.616137,1.049107,-1.983131
H,0,0.993707,-0.812982,-2.179655
H,0,-2.619596,1.784181,0.98658
H,0,-3.471004,1.107455,-0.398329
H,0,-2.207638,2.310542,-0.653011
N,0,1.918909,0.744044,0.459462
O,0,1.2209,0.687871,1.316574
O,0,2.680241,0.854522,-0.339724

meta N-Pi complex 190249
M062X/6-311G*
E(RM062X) = -476.295601518

Zero-point correction= 0.142032 (Hartree/Particle)
Thermal correction to Energy= 0.152141
Thermal correction to Enthalpy= 0.153085
Thermal correction to Gibbs Free Energy= 0.105353
Sum of electronic and ZPE= -476.153569
Sum of electronic and thermal Energies= -476.143461
Sum of electronic and thermal Enthalpies= -476.142517
Sum of electronic and thermal Free Energies= -476.190249

E CV S

KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.470 34.945 100.460

C,0,-0.136271,1.886722,-0.423211
C,0,0.772256,1.747752,0.623788
C,0,1.516614,0.578944,0.755274
C,0,1.376206,-0.477198,-0.151636
C,0,0.451762,-0.334854,-1.188327
C,0,-0.297207,0.839693,-1.327328
C,0,2.22012,-1.715703,-0.013173
H,0,-0.709923,2.799001,-0.535028
H,0,0.903263,2.551506,1.338924
H,0,2.225324,0.484091,1.571946
H,0,0.327116,-1.136455,-1.910156
H,0,-0.995145,0.9356,-2.152353
H,0,1.892094,-2.501416,-0.693542
H,0,2.185926,-2.104003,1.006613
H,0,3.264786,-1.489324,-0.239542
N,0,-1.909878,-0.623969,0.497401
O,0,-1.321272,-0.34124,1.391216
O,0,-2.571875,-0.94918,-0.331339

ortho N-Pi complex 189508
M062X/6-311G*
E(RM062X) = -476.295731534

Zero-point correction= 0.142352 (Hartree/Particle)
Thermal correction to Energy= 0.152324
Thermal correction to Enthalpy= 0.153268
Thermal correction to Gibbs Free Energy= 0.106224
Sum of electronic and ZPE= -476.153379
Sum of electronic and thermal Energies= -476.143408
Sum of electronic and thermal Enthalpies= -476.142463
Sum of electronic and thermal Free Energies= -476.189508

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.585 34.846 99.013

C,0,0.5562375542,1.6434878112,-0.167642926
C,0,0.2819617716,0.8575819862,-1.283383631
C,0,-0.7800371484,-0.053803273,-1.2570078873
C,0,-1.5880070585,-0.1874728055,-0.123999319
C,0,-1.2911580689,0.6016141734,0.9908897339
C,0,-0.2328371165,1.507272347,0.9719751166
C,0,-2.7649896336,-1.1257340309,-0.1110253199
H,0,1.3746199511,2.3532347205,-0.1864402328
H,0,0.8825659986,0.9568113219,-2.1811772917
H,0,-0.9962526403,-0.6494174421,-2.1391459789
H,0,-1.9008788738,0.5092648754,1.8839176639

H,0,-0.0247322701,2.1082354862,1.8496539776
H,0,-3.6864467213,-0.5754907572,-0.3174859129
H,0,-2.8806086296,-1.6034846318,0.8629653303
H,0,-2.666114218,-1.9027765478,-0.8696093477
N,0,1.3983159958,-1.5303244135,-0.0990032039
O,0,1.1979329044,-1.1561507012,0.9234101686
O,0,1.6671312034,-1.9776111189,-1.0783369397

ortho O-Pi complex 187442
M062X/6-311G*
E(RM062X) = -476.292124312

Zero-point correction= 0.142162 (Hartree/Particle)
Thermal correction to Energy= 0.152268
Thermal correction to Enthalpy= 0.153212
Thermal correction to Gibbs Free Energy= 0.104683
Sum of electronic and ZPE= -476.149962
Sum of electronic and thermal Energies= -476.139856
Sum of electronic and thermal Enthalpies= -476.138912
Sum of electronic and thermal Free Energies= -476.187442

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.550 34.690 102.139

C,0,-0.921954,1.93888,0.014999
C,0,-1.034305,1.250841,-1.19041
C,0,-1.208317,-0.131338,-1.193721
C,0,-1.275962,-0.850605,0.002837
C,0,-1.15797,-0.147722,1.206129
C,0,-0.984065,1.233882,1.21506
C,0,-1.509356,-2.338373,0.000606
H,0,-0.790806,3.014693,0.019528
H,0,-0.989538,1.790129,-2.129895
H,0,-1.299263,-0.658938,-2.13814
H,0,-1.209644,-0.689369,2.145702
H,0,-0.900236,1.759866,2.159474
H,0,-2.575877,-2.556187,0.102334
H,0,-0.997005,-2.823538,0.832923
H,0,-1.167918,-2.794483,-0.929531
N,0,2.542212,-0.118414,-0.017595
O,0,1.482637,0.199607,-0.03503
O,0,3.60316,-0.44294,0.001002

ortho O-Pi complex 187803
M062X/6-311G*
E(RM062X) = -476.292122761

Zero-point correction= 0.142106 (Hartree/Particle)
Thermal correction to Energy= 0.152247

Thermal correction to Enthalpy= 0.153192
Thermal correction to Gibbs Free Energy= 0.104320
Sum of electronic and ZPE= -476.150017
Sum of electronic and thermal Energies= -476.139875
Sum of electronic and thermal Enthalpies= -476.138931
Sum of electronic and thermal Free Energies= -476.187803

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.537 34.703 102.859

C,0,0.925866,1.938147,-0.005811
C,0,1.019102,1.245465,1.19851
C,0,1.19051,-0.1372,1.199127
C,0,1.274434,-0.852125,0.000982
C,0,1.175587,-0.144407,-1.201281
C,0,1.00459,1.237494,-1.207466
C,0,1.504895,-2.340377,0.000501
H,0,0.796481,3.014158,-0.008471
H,0,0.961436,1.781097,2.139407
H,0,1.266672,-0.6686,2.142707
H,0,1.240265,-0.68247,-2.14212
H,0,0.935772,1.767394,-2.150873
H,0,1.157842,-2.798258,0.927657
H,0,2.57145,-2.560157,-0.09658
H,0,0.995683,-2.822263,-0.835676
N,0,-2.542843,-0.115552,0.005189
O,0,-1.483369,0.203211,0.010074
O,0,-3.603581,-0.441213,-0.000042

para N-Pi complex 189915
M062X/6-311G*
E(RM062X) = -476.295984404

Zero-point correction= 0.141599 (Hartree/Particle)
Thermal correction to Energy= 0.150964
Thermal correction to Enthalpy= 0.151908
Thermal correction to Gibbs Free Energy= 0.106069
Sum of electronic and ZPE= -476.154386
Sum of electronic and thermal Energies= -476.145020
Sum of electronic and thermal Enthalpies= -476.144076
Sum of electronic and thermal Free Energies= -476.189915

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.731 33.128 96.476

C,0,-0.619284,1.588824,-0.108409
C,0,0.122251,1.410011,1.059896
C,0,1.217505,0.555026,1.061082

C,0,1.607116,-0.125408,-0.100793
C,0,0.864963,0.070472,-1.266805
C,0,-0.241909,0.91691,-1.274702
C,0,2.812738,-1.024983,-0.085461
H,0,-1.472228,2.258462,-0.117617
H,0,-0.158698,1.933239,1.966463
H,0,1.785167,0.410662,1.974851
H,0,1.154056,-0.442251,-2.178002
H,0,-0.800719,1.067728,-2.191798
H,0,3.728312,-0.430252,-0.034428
H,0,2.862371,-1.640641,-0.983509
H,0,2.802914,-1.68262,0.785654
N,0,-1.910165,-0.912844,0.208883
O,0,-1.021153,-1.413786,0.640268
O,0,-2.867633,-0.514905,-0.189349

para N-Pi complex 190032
M062X/6-311G*
E(RM062X) = -476.295972760

Zero-point correction= 0.142122 (Hartree/Particle)
Thermal correction to Energy= 0.152111
Thermal correction to Enthalpy= 0.153055
Thermal correction to Gibbs Free Energy= 0.105940
Sum of electronic and ZPE= -476.153851
Sum of electronic and thermal Energies= -476.143862
Sum of electronic and thermal Enthalpies= -476.142918
Sum of electronic and thermal Free Energies= -476.190032

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.451 34.938 99.161

C,0,-0.6388762601,1.5696736671,0.0040454767
C,0,-0.0753284116,1.1544719318,1.2115852809
C,0,1.0486367875,0.3329302965,1.2087953706
C,0,1.6320799698,-0.0824679734,0.008746454
C,0,1.0636843333,0.3505731406,-1.1956402649
C,0,-0.058387267,1.1699312136,-1.2033017963
C,0,2.8365655878,-0.9836878909,-0.0024101185
H,0,-1.5068904481,2.2202134349,0.0023552685
H,0,-0.5077693008,1.4781275452,2.1516031391
H,0,1.4816088099,0.0128507689,2.1507130514
H,0,1.512174078,0.0430889002,-2.1349790515
H,0,-0.4785841039,1.5064611117,-2.1443282528
H,0,2.5620655248,-1.9892016494,-0.332142453
H,0,3.28319924,-1.0645790799,0.9884021472
H,0,3.5945166451,-0.6108323663,-0.6935576987
N,0,-1.9270525762,-0.9506410492,-0.0075061625
O,0,-0.9967805058,-1.5515576504,-0.0110505825

O,0,-2.9179141027,-0.4497263512,-0.0051978077

para N-Pi complex 190293
M062X/6-311G*
E(RM062X) = -476.296006510

Zero-point correction= 0.141913 (Hartree/Particle)
Thermal correction to Energy= 0.151943
Thermal correction to Enthalpy= 0.152887
Thermal correction to Gibbs Free Energy= 0.105714
Sum of electronic and ZPE= -476.154094
Sum of electronic and thermal Energies= -476.144064
Sum of electronic and thermal Enthalpies= -476.143120
Sum of electronic and thermal Free Energies= -476.190293

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.346 35.032 99.284

C,0,0.629224,1.59598,-0.101083
C,0,0.247736,0.933174,-1.272232
C,0,-0.863614,0.094234,-1.269694
C,0,-1.605615,-0.107229,-0.103331
C,0,-1.215589,0.567167,1.060689
C,0,-0.114641,1.416387,1.064602
C,0,-2.78129,-1.045524,-0.087993
H,0,1.484514,2.262593,-0.106933
H,0,0.805993,1.089298,-2.188768
H,0,-1.158993,-0.408296,-2.184742
H,0,-1.786958,0.425674,1.972382
H,0,0.16511,1.937224,1.972899
H,0,-3.550929,-0.701861,0.603923
H,0,-2.46936,-2.04276,0.235063
H,0,-3.224149,-1.142186,-1.07961
N,0,1.888091,-0.926765,0.207504
O,0,0.990675,-1.418441,0.632198
O,0,2.851934,-0.538742,-0.18501

TS for the migration of NO_2^+ from ipso to ortho
Scrf=(solvent=dichloromethane)
m062x/6-311G*
E(RM062X) = -476.302669724

Zero-point correction= 0.141605 (Hartree/Particle)
Thermal correction to Energy= 0.150243
Thermal correction to Enthalpy= 0.151188
Thermal correction to Gibbs Free Energy= 0.108239
Sum of electronic and ZPE= -476.161065

Sum of electronic and thermal Energies= -476.152426
Sum of electronic and thermal Enthalpies= -476.151482
Sum of electronic and thermal Free Energies= -476.194431

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.279 32.609 90.393

C,0,0.1719202161,0.5186216559,0.1194991911
C,0,0.2052091644,0.2401799303,1.5321778975
C,0,1.3908187831,-0.1438193477,2.1649975075
C,0,2.5164779705,-0.3391461263,1.3975337687
C,0,2.5006535919,-0.0849774777,-0.000500622
C,0,1.3645681283,0.361755791,-0.6235817863
H,0,-0.7024120498,0.3902473263,2.1078705062
H,0,1.3997029568,-0.3266375682,3.2312600527
H,0,3.4346139323,-0.6834264978,1.8580302445
H,0,3.4087890605,-0.2357292737,-0.5711589485
C,0,-1.048645912,1.1112253491,-0.4940469319
N,0,-0.3763519628,-1.5945512614,0.4350723136
H,0,-1.9554269383,0.8305419608,0.0417133385
H,0,-0.9591030465,2.2008131442,-0.4238118605
H,0,-1.1397541357,0.8469332254,-1.5469306938
O,0,-1.5347204034,-1.6216534966,0.3596449594
O,0,0.5334658982,-2.3052120233,0.3816892307
H,0,1.3583977465,0.5825146898,-1.6841041673

TSs and CVTSs for Toluene + $NO_2^+BF_4^-$ ONIOM(M062X/6-311G*:PM3)/PCM(CH_2Cl_2)
TS NO_2BF_4 PCM ONIOM 2.596_9401
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.276289546170

Zero-point correction= 0.156550 (Hartree/Particle)
Thermal correction to Energy= 0.173208
Thermal correction to Enthalpy= 0.174153
Thermal correction to Gibbs Free Energy= 0.105710
Sum of electronic and ZPE= -476.889342
Sum of electronic and thermal Energies= -476.872684
Sum of electronic and thermal Enthalpies= -476.871740
Sum of electronic and thermal Free Energies= -476.940182

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.690 54.241 144.049

C,0,-2.6750868221,-1.4450653026,0.9828832779
C,0,-2.5040158475,-0.2625959191,1.7089629213
C,0,-2.9659197248,0.9336015956,1.1861691486
C,0,-3.6356270313,0.978620074,-0.0500217921
C,0,-3.8424005293,-0.2139864295,-0.7457798979

C,0,-3.3616106466,-1.4175909998,-0.2431453722
C,0,-4.0944536161,2.2940543599,-0.6092199975
H,0,-2.3182803499,-2.3878800668,1.3827134923
H,0,-1.9966904161,-0.2824724102,2.6660905215
H,0,-2.8128539199,1.8566838461,1.7354393182
H,0,-4.3738275336,-0.1990210904,-1.6908384857
H,0,-3.5249027646,-2.3403893541,-0.7885766553
H,0,-3.2536472815,2.8199896921,-1.0710205756
H,0,-4.48886255,2.9384181701,0.1775894623
H,0,-4.8626986396,2.1584178923,-1.3699058876
N,0,-0.7230961856,-0.9221129588,-0.6475052607
O,0,-0.8577705552,0.1797627829,-0.7745931324
O,0,-0.3091521567,-1.9636809271,-0.689433912
F,0,3.6345058339,-0.678394182,-0.6012902021
B,0,4.4043348073,0.2674850522,0.0445426799
F,0,5.3512354381,-0.3638945191,0.823102373
F,0,5.0284029508,1.0664143303,-0.8904072038
F,0,3.5940685401,1.044987364,0.84647118

TS NO_2BF_4 PCM ONIOM 2.605_94107
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.276199237599

Zero-point correction= 0.156724 (Hartree/Particle)
Thermal correction to Energy= 0.173431
Thermal correction to Enthalpy= 0.174375
Thermal correction to Gibbs Free Energy= 0.104649
Sum of electronic and ZPE= -476.889068
Sum of electronic and thermal Energies= -476.872361
Sum of electronic and thermal Enthalpies= -476.871417
Sum of electronic and thermal Free Energies= -476.941143

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.830 54.230 146.751

C,0,-2.2669844045,-0.9912855138,1.4162855093
C,0,-1.6531620259,0.2539137337,1.5801027024
C,0,-2.0729649762,1.3292075432,0.8146072886
C,0,-3.131470379,1.2026068148,-0.103427409
C,0,-3.7648748462,-0.0345772069,-0.2302321635
C,0,-3.3363489235,-1.1276544078,0.5148664178
C,0,-3.5805488844,2.3926487205,-0.9015632609
H,0,-1.947642179,-1.8409397423,2.0097141152
H,0,-0.8417093879,0.3702544115,2.288543254
H,0,-1.5805447968,2.2903776473,0.9206664874
H,0,-4.5882807817,-0.1478398962,-0.926440983
H,0,-3.8313156484,-2.086678476,0.4091663052
H,0,-4.203258574,3.0430821593,-0.2811859366

H,0,-4.1677465731,2.0953466686,-1.7699655222
H,0,-2.7278383181,2.9837593653,-1.2389958367
N,0,-1.0127362199,-1.5370397775,-0.8012895032
O,0,-0.8466721162,-2.625438221,-0.5878976788
O,0,-0.9788531623,-0.521766717,-1.2654073403
F,0,3.0720407201,-0.3664111865,-0.7720125981
B,0,4.0123538479,0.2706131387,0.0118743057
F,0,4.7894432063,-0.6727870397,0.6508763568
F,0,4.8097315258,1.0663826949,-0.7834376731
F,0,3.3710968969,1.0517912867,0.950912163

TS NO_2BF_4 PCM ONIOM 2.607_93956
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.275743056438

Zero-point correction= 0.157050 (Hartree/Particle)
Thermal correction to Energy= 0.173587
Thermal correction to Enthalpy= 0.174531
Thermal correction to Gibbs Free Energy= 0.106233
Sum of electronic and ZPE= -476.888744
Sum of electronic and thermal Energies= -476.872207
Sum of electronic and thermal Enthalpies= -476.871263
Sum of electronic and thermal Free Energies= -476.939561

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	108.928	54.104	143.745

C,0,-2.9533365588,-1.2001956215,1.0391206817
C,0,-2.346265656,-0.1367943783,1.7150542644
C,0,-2.3306145992,1.1212256158,1.1377236552
C,0,-2.9433287343,1.3604463597,-0.1063746993
C,0,-3.5839209018,0.3023921787,-0.7526108366
C,0,-3.5866730989,-0.9707455506,-0.1932185255
C,0,-2.8942365383,2.7328469908,-0.7130966515
H,0,-2.9734796907,-2.1896378522,1.4822446976
H,0,-1.8763771925,-0.3024566631,2.6772381666
H,0,-1.8384622263,1.9425286337,1.6488192907
H,0,-4.0734021437,0.4721701504,-1.7051098672
H,0,-4.0865760538,-1.7875678505,-0.7018994828
H,0,-3.2753171097,3.4773956171,-0.0111303028
H,0,-3.4818277691,2.7863768581,-1.6287471509
H,0,-1.8632627115,3.0085621276,-0.9499014719
N,0,-0.9498472462,-1.5123785781,-0.6003474817
O,0,-0.6727150649,-0.4448722443,-0.7733649719
O,0,-0.9562858454,-2.6335296065,-0.5919091797
F,0,3.1203605941,0.8314416412,0.8176231126
B,0,4.0735292224,0.2099035439,0.0373069546
F,0,4.8451401581,1.1616151532,-0.5953012429
F,0,4.8740321896,-0.5806311744,0.8352334436

F,0,3.4481169769,-0.5787903508,-0.9067994022

TS NO_2BF_4 PCM ONIOM 2.609_93861
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.276187286919

Zero-point correction= 0.156846 (Hartree/Particle)
Thermal correction to Energy= 0.173315
Thermal correction to Enthalpy= 0.174259
Thermal correction to Gibbs Free Energy= 0.107775
Sum of electronic and ZPE= -476.889544
Sum of electronic and thermal Energies= -476.873075
Sum of electronic and thermal Enthalpies= -476.872131
Sum of electronic and thermal Free Energies= -476.938616

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.757 54.156 139.928

C,0,-1.141141,0.34911,1.435769
C,0,-2.446576,0.859763,1.34469
C,0,-3.412049,0.181075,0.607708
C,0,-3.092585,-1.000356,-0.060814
C,0,-1.784618,-1.507821,0.050302
C,0,-0.822272,-0.855222,0.801951
C,0,-4.108618,-1.731236,-0.890524
H,0,-0.395888,0.868413,2.028154
H,0,-2.702367,1.77737,1.862753
H,0,-4.4185,0.579074,0.544542
H,0,-1.532957,-2.430206,-0.462876
H,0,0.179544,-1.263401,0.883707
H,0,-3.826679,-1.709787,-1.946517
H,0,-5.099355,-1.289388,-0.791559
H,0,-4.164384,-2.780222,-0.592394
N,0,-1.006739,1.76587,-0.75135
O,0,-1.407796,1.024254,-1.484012
O,0,-0.539607,2.674689,-0.290257
F,0,3.485517,0.469511,1.079387
B,0,3.54916,-0.329812,-0.043275
F,0,4.799774,-0.90264,-0.136114
F,0,2.593724,-1.321434,0.042984
F,0,3.308576,0.440417,-1.162959

CVTS NO_2BF_4 PCM ONIOM 940511
ONIOM(M062X/6-311G*:PM3)

Zero-point correction= 0.157810 (Hartree/Particle)
Thermal correction to Energy= 0.173570
Thermal correction to Enthalpy= 0.174514
Thermal correction to Gibbs Free Energy= 0.113420

Sum of electronic and ZPE= -476.896120
Sum of electronic and thermal Energies= -476.880361
Sum of electronic and thermal Enthalpies= -476.879417
Sum of electronic and thermal Free Energies= -476.940511

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.917 53.889 128.583

C,0,1.7726430496,2.5274859545,0.240607936
C,0,2.8292589405,1.7903559498,0.7792647208
C,0,3.0323207689,0.4751898159,0.3877278275
C,0,2.1811200223,-0.1324809068,-0.5511615161
C,0,1.120903404,0.6232021886,-1.0843309495
C,0,0.923467677,1.9435074253,-0.6962544567
C,0,2.4119857903,-1.5483440568,-0.995604446
H,0,1.6124348637,3.5519354883,0.5533989076
H,0,3.4883825545,2.2441521946,1.5090553414
H,0,3.8559738788,-0.0947654829,0.8035006892
H,0,0.4372075869,0.1578963808,-1.7922498013
H,0,0.0971893364,2.5085782374,-1.1099938065
H,0,1.4849672211,-2.0258494483,-1.3219437276
H,0,2.8623115577,-2.1502267662,-0.2048005008
H,0,3.0975054607,-1.5611752144,-1.8470008158
N,0,0.3927626694,-0.5153161317,1.4621973487
O,0,0.3748899157,-1.616734835,1.2706915126
O,0,0.2697508018,0.5154684258,1.8694208377
F,0,-1.118223307,-1.9341451047,-1.1353371699
B,0,-2.1167102286,-0.9863438358,-1.0458060102
F,0,-1.8222726,-0.1757559868,0.0408847399
F,0,-2.1543965771,-0.2286247,-2.1938722023
F,0,-3.3316067866,-1.5998445914,-0.8441094589

CVTS NO_2BF_4 PCM ONIOM 940237 (**6c**‡)
ONIOM(M062X/6-311G*:PM3)

Zero-point correction= 0.157445 (Hartree/Particle)
Thermal correction to Energy= 0.173403
Thermal correction to Enthalpy= 0.174347
Thermal correction to Gibbs Free Energy= 0.111801
Sum of electronic and ZPE= -476.894592
Sum of electronic and thermal Energies= -476.878634
Sum of electronic and thermal Enthalpies= -476.877690
Sum of electronic and thermal Free Energies= -476.940237

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.812 53.944 131.641

6 1.162594 2.052032 0.027483

6 2.420896 1.786859 0.576235
6 3.108754 0.618414 0.257979
6 2.547968 -0.327074 -0.597824
6 1.260489 -0.067365 -1.114869
6 0.587322 1.128557 -0.829996
6 3.299343 -1.563081 -1.003210
1 0.639542 2.965705 0.279393
1 2.869039 2.501467 1.255678
1 4.089707 0.439999 0.683566
1 0.798385 -0.791333 -1.780470
1 -0.401359 1.298649 -1.247357
1 3.868666 -1.363493 -1.914962
1 2.623925 -2.392726 -1.217956
1 4.004169 -1.872292 -0.231650
7 0.364926 -1.033384 1.101319
8 -0.067757 -1.971783 0.658998
8 0.662400 -0.255219 1.849836
9 -1.977631 0.248247 0.949054
5 -2.747493 0.067043 -0.189773
9 -3.948033 -0.510810 0.152936
9 -2.966927 1.277723 -0.805782
9 -2.039679 -0.775329 -1.024216

TS NO_2BF_4 PCM ONIOM 2.609_94
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.276337070450

Zero-point correction= 0.156436 (Hartree/Particle)
Thermal correction to Energy= 0.173186
Thermal correction to Enthalpy= 0.174131
Thermal correction to Gibbs Free Energy= 0.104413
Sum of electronic and ZPE= -476.889365
Sum of electronic and thermal Energies= -476.872614
Sum of electronic and thermal Enthalpies= -476.871670
Sum of electronic and thermal Free Energies= -476.941388

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.676 54.278 146.734

C,0,-3.3094513666,-1.5601810401,0.1154391825
C,0,-3.5151836577,-0.7721911543,1.2507907225
C,0,-3.513809622,0.6076734124,1.1349944023
C,0,-3.3416619794,1.2365624301,-0.1126472721
C,0,-3.1801378907,0.4411558921,-1.2466085333
C,0,-3.1538260358,-0.9458405401,-1.1389322494
C,0,-3.3200758338,2.7353197005,-0.199059069
H,0,-3.3109278073,-2.641589153,0.192155557
H,0,-3.6584003652,-1.2395436347,2.2175987841
H,0,-3.6502059683,1.2220787223,2.0190580771

H,0,-3.0604484662,0.9070135916,-2.2185508049
H,0,-3.0261785813,-1.5572296931,-2.0256699005
H,0,-3.3873947169,3.0776907173,-1.2310299378
H,0,-2.3922981684,3.1260518242,0.2281196268
H,0,-4.1457446974,3.1692413714,0.3675634328
N,0,-0.7360338145,-1.1364852696,0.0225442567
O,0,-0.4392952885,-2.1639976787,-0.3153149728
O,0,-0.7072313714,-0.0867064979,0.4035093715
F,0,5.3613674993,-0.5403606028,-0.6226608844
B,0,4.4151476502,0.2310319945,0.0187303481
F,0,5.0405289368,1.1714819982,0.8099468911
F,0,3.6281475548,0.8676444416,-0.919099954
F,0,3.6219869904,-0.5781068319,0.8065769258

TS NO_2BF_4 PCM ONIOM 2.611_93953
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.276799127793

Zero-point correction= 0.157066 (Hartree/Particle)
Thermal correction to Energy= 0.173641
Thermal correction to Enthalpy= 0.174585
Thermal correction to Gibbs Free Energy= 0.106473
Sum of electronic and ZPE= -476.888948
Sum of electronic and thermal Energies= -476.872372
Sum of electronic and thermal Enthalpies= -476.871428
Sum of electronic and thermal Free Energies= -476.939540

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	108.961	54.150	143.354

C,0,-3.1851351685,-1.1370697472,-0.7819697525
C,0,-3.8692077091,-0.4981942687,0.2547543425
C,0,-3.5169693561,0.7922826011,0.6136403913
C,0,-2.5048364517,1.4918553414,-0.070406071
C,0,-1.8587510044,0.8629613648,-1.1344348395
C,0,-2.1831507088,-0.4442963687,-1.4846742468
C,0,-2.12610192,2.8795255219,0.3597490167
H,0,-3.4523393173,-2.1465603433,-1.0737960739
H,0,-4.6591283282,-1.0167380018,0.7843872428
H,0,-4.0309511305,1.2817616621,1.4343353411
H,0,-1.0866655126,1.3912550156,-1.6832062639
H,0,-1.6737569836,-0.9277320913,-2.3112885881
H,0,-1.495644503,2.83937431,1.2527257306
H,0,-3.0105892945,3.4661881024,0.6122874393
H,0,-1.570948711,3.4002711952,-0.4198908877
N,0,-1.0412025106,-1.6306214756,0.6241130087
O,0,-1.0628013505,-0.7450107001,1.3054428202
O,0,-0.7869000475,-2.6215025142,0.1634609924
F,0,4.6525434942,0.793887154,-0.9694176894

B,0,3.8683055771,0.1565381417,-0.0313856429
F,0,4.6582035447,-0.6441683714,0.7670079786
F,0,3.2279972937,1.0950580464,0.7514038404
F,0,2.926630098,-0.6233975742,-0.671230089

TS NO_2BF_4 PCM ONIOM 2.610_94049
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.276300266484

Zero-point correction= 0.156770 (Hartree/Particle)
Thermal correction to Energy= 0.173457
Thermal correction to Enthalpy= 0.174401
Thermal correction to Gibbs Free Energy= 0.105311
Sum of electronic and ZPE= -476.889033
Sum of electronic and thermal Energies= -476.872347
Sum of electronic and thermal Enthalpies= -476.871402
Sum of electronic and thermal Free Energies= -476.940492

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.846 54.161 145.412

C,0,3.3198182545,-1.5280803069,-0.1132524094
C,0,2.9719067116,-0.8256111231,-1.27927259
C,0,2.9397899672,0.565484325,-1.2741872659
C,0,3.2337573345,1.2761887374,-0.1108854678
C,0,3.5977537962,0.5603397676,1.0453403394
C,0,3.6577222184,-0.8229786235,1.0453922282
C,0,3.1586997358,2.7752383753,-0.0700338292
H,0,3.3641322821,-2.6112761288,-0.1270582991
H,0,2.7395505925,-1.3719831021,-2.1868802698
H,0,2.6721567015,1.1012645203,-2.1780927975
H,0,3.8371293035,1.110319138,1.9495903835
H,0,3.9477123575,-1.3585818856,1.9412153786
H,0,4.0673341382,3.1959436059,0.3646703164
H,0,2.3207966775,3.0969390806,0.5544206629
H,0,3.0215844359,3.1964107474,-1.0653830767
N,0,0.7468147841,-1.2027818039,0.1870762578
O,0,0.7419680947,-0.1834310153,0.6433888391
O,0,0.4388144602,-2.2171296846,-0.1787256487
F,0,-3.5420724644,1.0300567449,0.7932016532
B,0,-4.3410304182,0.2264406419,0.0059425192
F,0,-4.960182619,-0.7186799977,0.7970727562
F,0,-5.2920386999,0.9997334224,-0.6255031877
F,0,-3.5604406448,-0.4078154351,-0.9389304927

TS NO_2BF_4 PCM ONIOM 2.611_94056
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.276280398458

Zero-point correction= 0.156771 (Hartree/Particle)
Thermal correction to Energy= 0.173463
Thermal correction to Enthalpy= 0.174407
Thermal correction to Gibbs Free Energy= 0.105258
Sum of electronic and ZPE= -476.889047
Sum of electronic and thermal Energies= -476.872355
Sum of electronic and thermal Enthalpies= -476.871411
Sum of electronic and thermal Free Energies= -476.940560

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.849 54.163 145.536

C,0,-3.3290279452,-1.5307805045,0.1109179366
C,0,-2.982488655,-0.8286420044,1.2774981483
C,0,-2.9548030649,0.5626025638,1.274172895
C,0,-3.2517515046,1.2738220973,0.1119851672
C,0,-3.613932981,0.5582178572,-1.0449453384
C,0,-3.6695157217,-0.8253226567,-1.0466754257
C,0,-3.1822493898,2.7732113941,0.073111299
H,0,-3.3699318259,-2.6141156485,0.1233957854
H,0,-2.7479811535,-1.3753672985,2.1843378835
H,0,-2.6883904254,1.0980587989,2.1786313333
H,0,-3.855491916,1.1085382395,-1.9484150347
H,0,-3.9581645092,-1.3607136306,-1.9430598035
H,0,-3.042489102,3.193381995,1.0685144297
H,0,-4.094399018,3.1911624245,-0.3569107881
H,0,-2.3483899329,3.0990593793,-0.5545460943
N,0,-0.7558730041,-1.196076506,-0.1878797579
O,0,-0.75550337,-0.1777439524,-0.6463786961
O,0,-0.444127893,-2.2082912874,0.1804683732
F,0,4.9888115223,-0.5668055179,0.9356586827
B,0,4.3664399762,0.2256925513,-0.0061192261
F,0,5.3150634384,0.8757263133,-0.7668816158
F,0,3.5836674784,-0.5642269493,-0.8232907877
F,0,3.568896997,1.1541833421,0.6308886345

TS NO_2BF_4 PCM ONIOM 2.612_94115
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.276652314278

Zero-point correction= 0.156617 (Hartree/Particle)
Thermal correction to Energy= 0.173321
Thermal correction to Enthalpy= 0.174265
Thermal correction to Gibbs Free Energy= 0.104690
Sum of electronic and ZPE= -476.889231
Sum of electronic and thermal Energies= -476.872527
Sum of electronic and thermal Enthalpies= -476.871583
Sum of electronic and thermal Free Energies= -476.941158

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.761 54.240 146.433

C,0,3.1418573429,-1.6764251096,-0.1081662376
C,0,3.4765349531,-0.93414199,-1.2437926861
C,0,3.6761454128,0.4316301192,-1.1330827351
C,0,3.582661498,1.0870951755,0.1095264695
C,0,3.2897424431,0.3317740025,1.2438264442
C,0,3.0591833782,-1.03731418,1.140597703
C,0,3.7890541861,2.5723331009,0.1886468296
H,0,2.9858722967,-2.7471281749,-0.1798575458
H,0,3.5633500173,-1.4229373963,-2.2066265805
H,0,3.9143567299,1.0140456437,-2.0172183854
H,0,3.2256547884,0.8158436477,2.2120069836
H,0,2.8267880735,-1.6171314342,2.0272383772
H,0,2.9750389555,3.0969529478,-0.3188163622
H,0,4.7180151685,2.8603608466,-0.3072769205
H,0,3.8249377421,2.917257244,1.2212984227
N,0,0.6595530302,-0.8680306126,-0.0142666734
O,0,0.7883237896,0.1594232039,-0.434262599
O,0,0.209586049,-1.8249010913,0.3598425383
F,0,-5.13036512,-0.7037884801,0.76761482
B,0,-4.5066046067,0.2391749289,-0.0222856253
F,0,-5.45402977,1.0160925799,-0.6547432312
F,0,-3.7061051096,1.0402010708,0.766297609
F,0,-3.7270442487,-0.3972010425,-0.9665236153

TS NO_2BF_4 PCM ONIOM 2.613_94064
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.276431719226

Zero-point correction= 0.156537 (Hartree/Particle)
Thermal correction to Energy= 0.173222
Thermal correction to Enthalpy= 0.174166
Thermal correction to Gibbs Free Energy= 0.105269
Sum of electronic and ZPE= -476.889376
Sum of electronic and thermal Energies= -476.872691
Sum of electronic and thermal Enthalpies= -476.871747
Sum of electronic and thermal Free Energies= -476.940644

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.699 54.249 145.007

C,0,3.2075474601,-1.4794373705,0.5093753733
C,0,3.8406053965,-0.9263825442,-0.6068713694
C,0,3.7939571153,0.4423344726,-0.8111089998
C,0,3.1484185883,1.2964345822,0.1028102457
C,0,2.5554472671,0.7399803946,1.2351603782

C,0,2.5734037352,-0.6370250963,1.4377876942
C,0,3.1088966202,2.7750493447,-0.1554458275
H,0,3.238018329,-2.5494212882,0.6819221738
H,0,4.3496681382,-1.5681664432,-1.3155594877
H,0,4.2638578757,0.8728234762,-1.68941124
H,0,2.0644795358,1.3832600652,1.956913858
H,0,2.1092324719,-1.0624600785,2.3208426915
H,0,2.5598435044,2.9884712958,-1.0759538043
H,0,4.1190889244,3.1698193104,-0.2826941763
H,0,2.6283385073,3.3111673902,0.6621312335
N,0,0.7947262402,-1.2669586805,-0.4726651369
O,0,0.9199778838,-0.3304075092,-1.068463059
O,0,0.3891444682,-2.2203315048,-0.0438823771
F,0,-5.2100460273,-0.3964140215,0.7994704299
B,0,-4.2641704022,0.2311505713,0.0165443892
F,0,-4.8895509495,1.0300480945,-0.9174885275
F,0,-3.4490426321,1.0076869634,0.8145121064
F,0,-3.4992510506,-0.7181564244,-0.6301275681

TS NO_2BF_4 PCM ONIOM 2.613_94071
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.276821454218

Zero-point correction= 0.156423 (Hartree/Particle)
Thermal correction to Energy= 0.173140
Thermal correction to Enthalpy= 0.174084
Thermal correction to Gibbs Free Energy= 0.105191
Sum of electronic and ZPE= -476.889491
Sum of electronic and thermal Energies= -476.872774
Sum of electronic and thermal Enthalpies= -476.871830
Sum of electronic and thermal Free Energies= -476.940723

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.647 54.310 144.997

C,0,3.0224903345,-1.4263357801,0.7635508635
C,0,3.8550301339,-0.9749464128,-0.2633723677
C,0,3.8578583074,0.3679425871,-0.601687913
C,0,3.0627826395,1.2994864119,0.0923279105
C,0,2.2658275823,0.8465190361,1.142191704
C,0,2.2327955965,-0.5056392688,1.4725750561
C,0,3.0801712193,2.7463679762,-0.3087432271
H,0,3.0126219705,-2.4747817078,1.040055968
H,0,4.4816700033,-1.6751251481,-0.8021412307
H,0,4.486547015,0.7161517913,-1.4146770705
H,0,1.6556380442,1.5498835791,1.6979545513
H,0,1.6073290036,-0.8486781569,2.2896445963
H,0,2.5151111891,3.3614915846,0.3906382766
H,0,2.6438797503,2.8717747903,-1.3032447731

H,0,4.1040149503,3.1224806015,-0.3546812017
N,0,0.82391867,-1.3146699784,-0.6456226419
O,0,1.0829337801,-0.4590288523,-1.3157535668
O,0,0.3198220076,-2.2083923599,-0.1930486656
F,0,-3.3319368184,1.0327271952,0.8168214364
B,0,-4.1424033843,0.2393501755,0.0307931039
F,0,-5.0903237922,1.023613844,-0.5917835974
F,0,-3.372674073,-0.3964201888,-0.9219640871
F,0,-4.7653561295,-0.7043137187,0.8204098761

TS NO_2BF_4 PCM ONIOM 2.615_93981
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.276549001638

Zero-point correction= 0.157000 (Hartree/Particle)
Thermal correction to Energy= 0.173600
Thermal correction to Enthalpy= 0.174545
Thermal correction to Gibbs Free Energy= 0.106270
Sum of electronic and ZPE= -476.889079
Sum of electronic and thermal Energies= -476.872479
Sum of electronic and thermal Enthalpies= -476.871534
Sum of electronic and thermal Free Energies= -476.939809

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.936 54.169 143.695

C,0,3.1196291982,-1.0808566656,0.8080661191
C,0,3.7985115228,-0.4226485134,-0.2204279618
C,0,3.4026591545,0.8498516611,-0.5967407263
C,0,2.3489746754,1.5137491368,0.0605114995
C,0,1.7029568685,0.8647695748,1.111529413
C,0,2.0736508322,-0.4257038764,1.4803448496
C,0,1.941791196,2.8910005313,-0.3778143084
H,0,3.4219625001,-2.075619746,1.1152601751
H,0,4.6189361356,-0.9131240327,-0.7300387553
H,0,3.9145381098,1.3539158729,-1.4100582988
H,0,0.8965857839,1.363629141,1.6379740843
H,0,1.5654742515,-0.9230810774,2.2994573387
H,0,2.807601422,3.5552922789,-0.4131860066
H,0,1.2015711975,3.3214271574,0.2957237416
H,0,1.5143785617,2.8611657411,-1.3834551806
N,0,1.0219673041,-1.6849087066,-0.6318777582
O,0,1.0275033153,-0.8113089123,-1.3282589771
O,0,0.7981750005,-2.6756490282,-0.1561079368
F,0,-2.927252812,-0.4902361943,0.9725884872
B,0,-3.7106899216,0.147416636,0.0323470408
F,0,-4.3258879968,-0.7956109265,-0.7646074416
F,0,-4.6649648154,0.9126932271,0.6684029762
F,0,-2.9148494839,0.9583627209,-0.7504803736

TS NO_2BF_4 PCM ONIOM 2.622_94034
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.276107961845

Zero-point correction= 0.156649 (Hartree/Particle)
Thermal correction to Energy= 0.173357
Thermal correction to Enthalpy= 0.174302
Thermal correction to Gibbs Free Energy= 0.105680
Sum of electronic and ZPE= -476.889379
Sum of electronic and thermal Energies= -476.872670
Sum of electronic and thermal Enthalpies= -476.871726
Sum of electronic and thermal Free Energies= -476.940348

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.783 54.263 144.427

C,0,3.3948242133,-0.8389460343,0.6037496846
C,0,3.7721539307,-0.0666775372,-0.4973071118
C,0,3.1079355413,1.1198846919,-0.7606445035
C,0,2.0777848345,1.5844757159,0.0785899169
C,0,1.7346063819,0.8267338107,1.1973900247
C,0,2.3772500919,-0.3810001995,1.4572450621
C,0,1.3734327192,2.8710879859,-0.2434363144
H,0,3.907835837,-1.7686402366,0.8224163757
H,0,4.5691274989,-0.4031991637,-1.149044871
H,0,3.3853369834,1.7098321009,-1.6282818991
H,0,0.9522513046,1.173543422,1.8634870744
H,0,2.1027057769,-0.9649724716,2.3291172233
H,0,0.6774999295,3.1545490591,0.5452056759
H,0,0.8137067586,2.7774017282,-1.1776059465
H,0,2.094095311,3.6801577302,-0.3782249101
N,0,1.2120651589,-1.777031207,-0.5071644015
O,0,1.2381728141,-2.7932986149,-0.0347681514
O,0,0.9631084816,-0.9062733554,-1.1598973717
F,0,-4.6528966211,0.6911334075,0.7842058976
B,0,-3.7002073634,0.0495005246,0.0214102305
F,0,-2.9064324461,0.9844139664,-0.6102517746
F,0,-2.9147686012,-0.7413766948,0.83530138
F,0,-4.3180095353,-0.7416496284,-0.9247892903

TS NO_2BF_4 PCM ONIOM 2.629_93709
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.276064279501

Zero-point correction= 0.157132 (Hartree/Particle)
Thermal correction to Energy= 0.173324
Thermal correction to Enthalpy= 0.174268
Thermal correction to Gibbs Free Energy= 0.110282

Sum of electronic and ZPE= -476.890187
Sum of electronic and thermal Energies= -476.873995
Sum of electronic and thermal Enthalpies= -476.873051
Sum of electronic and thermal Free Energies= -476.937037

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.763 54.005 134.671

C,0,-2.7170462734,-0.2931307136,1.263782627
C,0,-1.3163721188,-0.340497541,1.3670979738
C,0,-0.5317036628,0.6062740058,0.7137601153
C,0,-1.1237923323,1.5997194367,-0.0645095098
C,0,-2.5277503934,1.6427183476,-0.1488893955
C,0,-3.3189955139,0.7204780963,0.5166900268
C,0,-0.2952446922,2.6204416713,-0.7904444944
H,0,-3.3235841378,-1.0217112166,1.7895297544
H,0,-0.8459819185,-1.1120653305,1.9670876845
H,0,0.5531532266,0.5528335885,0.7890910265
H,0,-2.9939689007,2.4170263624,-0.7491131178
H,0,-4.3983331205,0.7744119775,0.4444080357
H,0,-0.3744829626,3.5911683855,-0.2941882526
H,0,-0.6449522602,2.7496387761,-1.816178538
H,0,0.7573828297,2.336167493,-0.8134878494
N,0,-1.9630654861,-1.729572798,-0.8059289005
O,0,-1.8408432789,-0.9069040518,-1.5506837675
O,0,-2.0689855834,-2.7368849573,-0.3255847113
F,0,3.1532528531,0.7755089808,1.0269810754
B,0,3.1026883565,-0.2014699505,0.054469445
F,0,4.3854656577,-0.5713058083,-0.2926584696
F,0,2.4277354348,-1.3034037357,0.5407803481
F,0,2.451556277,0.2823699818,-1.0621381061

TS NO_2BF_4 PCM ONIOM 2.635_93808
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.275285670989

Zero-point correction= 0.157062 (Hartree/Particle)
Thermal correction to Energy= 0.173401
Thermal correction to Enthalpy= 0.174345
Thermal correction to Gibbs Free Energy= 0.108630
Sum of electronic and ZPE= -476.889651
Sum of electronic and thermal Energies= -476.873312
Sum of electronic and thermal Enthalpies= -476.872368
Sum of electronic and thermal Free Energies= -476.938082

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.811 54.069 138.308

C,0,-1.368715425,0.663147184,1.4948294022
C,0,-2.765110848,0.6942260621,1.4473503522
C,0,-3.4439236979,-0.2140282207,0.6519093833
C,0,-2.7562304148,-1.1916017019,-0.0893704684
C,0,-1.3648433836,-1.2366447511,-0.0078228458
C,0,-0.6704801596,-0.3146936256,0.7699612437
C,0,-3.5210641608,-2.1574289553,-0.9483776656
H,0,-0.825940152,1.3665601541,2.1162379102
H,0,-3.3110081344,1.4342093866,2.0197650272
H,0,-4.5271540055,-0.1793620431,0.5992941311
H,0,-0.8171913522,-1.9917697755,-0.5609707996
H,0,0.4151440785,-0.3581138695,0.823231277
H,0,-4.0171823936,-1.631651269,-1.7681181132
H,0,-4.2985913736,-2.6575619327,-0.3675714794
H,0,-2.8663557281,-2.9160867434,-1.3756685536
N,0,-1.0708340577,1.8293555623,-0.8501019731
O,0,-0.1976994675,2.4632723305,-0.5533856607
O,0,-1.9367653842,1.3738866243,-1.3860390643
F,0,2.8100212727,0.4685828514,0.937681276
B,0,3.4187055443,-0.3436897351,0.0031481093
F,0,4.2003192678,-1.2811119331,0.6447433902
F,0,2.4567070139,-0.9832214934,-0.7516714197
F,0,4.2074949614,0.428416894,-0.824636459

TS NO_2BF_4 PCM ONIOM 2.677_94011
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.277990728277

Zero-point correction= 0.157761 (Hartree/Particle)
Thermal correction to Energy= 0.173818
Thermal correction to Enthalpy= 0.174763
Thermal correction to Gibbs Free Energy= 0.111701
Sum of electronic and ZPE= -476.894037
Sum of electronic and thermal Energies= -476.877980
Sum of electronic and thermal Enthalpies= -476.877036
Sum of electronic and thermal Free Energies= -476.940097

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.073 53.859 132.724

C,0,-1.0167931141,0.6546539756,1.52626604
C,0,-2.2990088058,1.0955655399,1.1690867471
C,0,-3.1170585723,0.2913891123,0.3855843569
C,0,-2.6766441813,-0.9592999878,-0.0591211476
C,0,-1.3973484339,-1.3933992,0.3152810796
C,0,-0.5750966505,-0.6028718646,1.1071760951
C,0,-3.5430288791,-1.8106946082,-0.9437312266
H,0,-0.3811942374,1.2760124438,2.1475500179
H,0,-2.6542185414,2.0591747718,1.5157718749

H,0,-4.1081653425,0.6364115615,0.1125184195
H,0,-1.0453509355,-2.361810367,-0.0238930574
H,0,0.4224270008,-0.9448522609,1.370964448
H,0,-3.3321439386,-1.5997566066,-1.9962107429
H,0,-4.6009209354,-1.6119900618,-0.7715251193
H,0,-3.3547284525,-2.8715408394,-0.7768710517
N,0,-0.408345002,1.6853649948,-0.8696071573
O,0,0.0884334374,2.5856723793,-0.4331813499
O,0,-0.8312157186,0.887663773,-1.5200562673
F,0,2.4643425372,-1.7621210008,-0.1613232214
B,0,2.8234332436,-0.4402276232,-0.0176409319
F,0,2.9676520273,-0.1341389008,1.3177089518
F,0,4.0078924533,-0.2078779038,-0.6812561056
F,0,1.8363940412,0.3665336728,-0.5652726519

TS NO_2BF_4 PCM ONIOM 2.682_93941
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.277735092828

Zero-point correction= 0.158019 (Hartree/Particle)
Thermal correction to Energy= 0.173952
Thermal correction to Enthalpy= 0.174897
Thermal correction to Gibbs Free Energy= 0.112396
Sum of electronic and ZPE= -476.893796
Sum of electronic and thermal Energies= -476.877863
Sum of electronic and thermal Enthalpies= -476.876919
Sum of electronic and thermal Free Energies= -476.939419

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.157 53.774 131.543

C,0,-1.0207411657,0.6534675118,1.5263236065
C,0,-2.2994375449,1.0973039372,1.1654703933
C,0,-3.117590623,0.2953410304,0.3770750003
C,0,-2.6788048175,-0.9542082167,-0.0673439985
C,0,-1.3997246597,-1.3911406695,0.3095809906
C,0,-0.579285103,-0.6046811057,1.1052253285
C,0,-3.5440513631,-1.8218325778,-0.9372420806
H,0,-0.3853208824,1.2728916106,2.1497339728
H,0,-2.6537458569,2.0616602361,1.5110485606
H,0,-4.1063061267,0.6437191132,0.1006015769
H,0,-1.0483100067,-2.3587783708,-0.0332194102
H,0,0.4177655663,-0.9476179631,1.3695793122
H,0,-4.5305260858,-1.3830793431,-1.0834829269
H,0,-3.6682801604,-2.8108144532,-0.4913803389
H,0,-3.0834922845,-1.9645120946,-1.9179770629
N,0,-0.4032232657,1.6936065265,-0.8701806119
O,0,0.0906409865,2.592535309,-0.4281434221

O,0,-0.8223463573,0.8953343874,-1.5219544042
F,0,4.0091640572,-0.211715705,-0.6754599702
B,0,2.8224784046,-0.4421480664,-0.0151514308
F,0,2.4577728085,-1.7616615465,-0.1664147733
F,0,2.9657560083,-0.1437782211,1.3220459733
F,0,1.8400964721,0.3719026714,-0.5603382845

TS NO_2BF_4 PCM ONIOM 2.684_93988
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.277678376338

Zero-point correction= 0.157775 (Hartree/Particle)
Thermal correction to Energy= 0.173751
Thermal correction to Enthalpy= 0.174696
Thermal correction to Gibbs Free Energy= 0.111918
Sum of electronic and ZPE= -476.894012
Sum of electronic and thermal Energies= -476.878036
Sum of electronic and thermal Enthalpies= -476.877092
Sum of electronic and thermal Free Energies= -476.939870

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.031 53.837 132.127

C,0,-1.0149183164,0.6485224514,1.5297841378
C,0,-2.2944213392,1.094042334,1.1724346355
C,0,-3.1149385925,0.2938705021,0.3855385963
C,0,-2.6781717096,-0.9559204435,-0.0618921704
C,0,-1.3998088571,-1.3950904181,0.3127645785
C,0,-0.5762896707,-0.6095674403,1.1071728457
C,0,-3.5425641648,-1.8097925219,-0.9460411757
H,0,-0.3775723186,1.2666285275,2.1525242999
H,0,-2.6472572039,2.0580184107,1.5205826672
H,0,-4.104436673,0.643068586,0.1125816311
H,0,-1.0506451487,-2.3635641831,-0.0297675655
H,0,0.4204241034,-0.9545317226,1.3701481197
H,0,-3.5062986754,-2.8550430398,-0.6353981227
H,0,-3.1901909069,-1.7647239458,-1.9802922249
H,0,-4.5801883673,-1.4775282543,-0.9298705636
N,0,-0.4075657098,1.6882032406,-0.873354704
O,0,0.0854516011,2.5883823289,-0.4333203468
O,0,-0.8280881043,0.8876088521,-1.5211790391
F,0,1.8359087115,0.368621953,-0.5644665109
B,0,2.8222728194,-0.4385707053,-0.0162447601
F,0,2.4638958027,-1.7604313923,-0.162030013
F,0,4.0077098316,-0.2051368112,-0.6777531851
F,0,2.9643388885,-0.1339953082,1.31967987

TS NO_2BF_4 PCM ONIOM 2.693_94047
ONIOM(M062X/6-311G*:PM3)

E(RPM3) = 0.278733764858

Zero-point correction= 0.157605 (Hartree/Particle)
Thermal correction to Energy= 0.173752
Thermal correction to Enthalpy= 0.174697
Thermal correction to Gibbs Free Energy= 0.110995
Sum of electronic and ZPE= -476.893866
Sum of electronic and thermal Energies= -476.877718
Sum of electronic and thermal Enthalpies= -476.876774
Sum of electronic and thermal Free Energies= -476.940476

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.031 53.909 134.071

C,0,-1.9710484295,-1.1388058593,-1.2792846128
C,0,-3.1092259835,-0.7678585052,-0.5612491217
C,0,-3.1486081812,0.4616202217,0.0795415164
C,0,-2.0688343092,1.3564459554,0.0061755954
C,0,-0.9478050077,0.9894850043,-0.7403880898
C,0,-0.8917428627,-0.2479391618,-1.374923141
C,0,-2.1209628474,2.6672139285,0.7386932447
H,0,-1.9308322235,-2.0964383566,-1.7857098687
H,0,-3.9545498644,-1.4421040755,-0.4986009583
H,0,-4.0276472368,0.7422789257,0.6500516451
H,0,-0.0955227686,1.6598748122,-0.8035738181
H,0,-0.0057241961,-0.5256650632,-1.9369433534
H,0,-1.3784764944,3.3668556811,0.3556763072
H,0,-1.9222663533,2.5150758191,1.803258911
H,0,-3.1078240187,3.1242039094,0.652305364
N,0,-0.5299459837,-1.6993452272,0.9264021151
O,0,-0.9406385848,-0.9067382833,1.5918059868
O,0,-0.0243222606,-2.5923275535,0.4834354033
F,0,1.632626258,-0.3080600916,0.4256453401
B,0,2.7692503742,0.3130130217,-0.0702201201
F,0,3.2144796789,-0.3814783983,-1.1736185876
F,0,2.4728009674,1.6109391124,-0.422367258
F,0,3.7419973274,0.3077401841,0.9057085004

TS NO_2BF_4 PCM ONIOM 2.701_94088
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.278953217307

Zero-point correction= 0.157420 (Hartree/Particle)
Thermal correction to Energy= 0.173557
Thermal correction to Enthalpy= 0.174501
Thermal correction to Gibbs Free Energy= 0.110945
Sum of electronic and ZPE= -476.894402
Sum of electronic and thermal Energies= -476.878265
Sum of electronic and thermal Enthalpies= -476.877321

Sum of electronic and thermal Free Energies= -476.940877

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.909 53.925 133.764

C,0,1.9765542662,-1.0795331913,1.2912844969
C,0,3.0913080629,-0.6243938626,0.5854724117
C,0,3.0405650283,0.5963925347,-0.0703197674
C,0,1.8901834759,1.402719156,-0.0250441598
C,0,0.7907174647,0.9514768017,0.7041431096
C,0,0.8260611657,-0.2797700687,1.3544350618
C,0,1.8632781214,2.7182666793,-0.7502434448
H,0,2.0061095431,-2.0318374001,1.8080714397
H,0,3.9893211564,-1.2284939134,0.5425322621
H,0,3.9026233158,0.9400344144,-0.6326083896
H,0,-0.1210671873,1.5426124855,0.7390806288
H,0,-0.0486638354,-0.6208284268,1.9010953363
H,0,2.6391965208,3.3831178385,-0.3643454733
H,0,0.9001434398,3.2150698863,-0.6378957523
H,0,2.0567570382,2.577105315,-1.8159137816
N,0,0.5794721697,-1.762734616,-0.9185829284
O,0,0.9777948632,-0.9749079694,-1.5971888283
O,0,0.0986779013,-2.6637438864,-0.4640688699
F,0,-2.5057061004,0.2193259369,1.4408649788
B,0,-2.6579664105,0.2875306978,0.0734703039
F,0,-2.5456307729,1.5937726518,-0.3490189358
F,0,-1.6750884126,-0.4780040949,-0.537532773
F,0,-3.8928848142,-0.2106219683,-0.2795919255

TS NO_2BF_4 PCM ONIOM 2.704_94050
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.278838719430

Zero-point correction= 0.157559 (Hartree/Particle)
Thermal correction to Energy= 0.173652
Thermal correction to Enthalpy= 0.174597
Thermal correction to Gibbs Free Energy= 0.111322
Sum of electronic and ZPE= -476.894264
Sum of electronic and thermal Energies= -476.878170
Sum of electronic and thermal Enthalpies= -476.877226
Sum of electronic and thermal Free Energies= -476.940501

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.969 53.894 133.174

C,0,1.9715952026,-1.0799432063,-1.2941516224
C,0,0.8229693975,-0.2773893443,-1.3561354884
C,0,0.7915618952,0.9540926975,-0.7064387747

C,0,1.8932394482,1.4030311879,0.0212537759
C,0,3.0416054174,0.594147815,0.0650867954
C,0,3.0883277884,-0.6272858636,-0.5900710785
C,0,1.8651580401,2.7132307959,0.7561970318
H,0,1.9985481718,-2.0320030507,-1.8115216483
H,0,-0.0528564376,-0.6161938028,-1.9024086211
H,0,-0.1183115953,1.5481562199,-0.7414009548
H,0,3.9059405518,0.9365139214,0.6245620208
H,0,3.9854395915,-1.2328732011,-0.5492166902
H,0,1.8869622149,2.5482353827,1.8363951944
H,0,0.9686034973,3.2844495215,0.5172825847
H,0,2.7382705583,3.3170470902,0.5017316922
N,0,0.5806384726,-1.7596743155,0.9228404845
O,0,0.9788379699,-0.9684788417,1.5973835391
O,0,0.1010570164,-2.6621227139,0.4703235097
F,0,-1.6736620529,-0.4775328617,0.5364412099
B,0,-2.6579110368,0.2868604786,-0.0737736271
F,0,-2.5459789371,1.5933942414,0.3478953663
F,0,-2.5075163205,0.2182343619,-1.4413443418
F,0,-3.8919528537,-0.2121695124,0.2811446426

TS NO_2BF_4 PCM ONIOM 2.707_94118 (**6b**‡)
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.279306447119

Zero-point correction= 0.157378 (Hartree/Particle)
Thermal correction to Energy= 0.173583
Thermal correction to Enthalpy= 0.174528
Thermal correction to Gibbs Free Energy= 0.110257
Sum of electronic and ZPE= -476.894062
Sum of electronic and thermal Energies= -476.877857
Sum of electronic and thermal Enthalpies= -476.876912
Sum of electronic and thermal Free Energies= -476.941183

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.925 54.011 135.269

C,0,2.3215255531,-1.0762211587,1.1383689184
C,0,3.270536233,-0.5009921066,0.2930659736
C,0,3.02550623,0.7417530586,-0.2725311943
C,0,1.8456986966,1.4524578568,0.0066482872
C,0,0.9168480258,0.8833693305,0.8768664558
C,0,1.1432523001,-0.3739016818,1.4333679999
C,0,1.6019405633,2.7902196422,-0.6328861843
H,0,2.5007259598,-2.0473157729,1.5854871041
H,0,4.1892151072,-1.0289619709,0.0688546777
H,0,3.7559535961,1.1782534454,-0.9457960294
H,0,-0.0103779224,1.4045641726,1.0974265787
H,0,0.4027608163,-0.8093525217,2.0960194833

H,0,2.4276919562,3.4734350406,-0.4243457612
H,0,0.6800288602,3.2426982856,-0.2690482559
H,0,1.5290206364,2.6899341734,-1.7186168035
N,0,0.6044614291,-1.7295835898,-0.8495629621
O,0,0.8948576018,-0.9166578677,-1.5533535414
O,0,0.2023369755,-2.6541150058,-0.3657284551
F,0,-2.5797991112,0.9922755677,1.1987205634
B,0,-2.7654216009,0.2255606728,0.0696923816
F,0,-3.8118480238,-0.6477883708,0.2697760571
F,0,-3.0388137881,1.0400672759,-1.0073135994
F,0,-1.6147580941,-0.5019934753,-0.1941886943

TS NO_2BF_4 PCM ONIOM 2.712_94072
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.278797036640

Zero-point correction= 0.157425 (Hartree/Particle)
Thermal correction to Energy= 0.173604
Thermal correction to Enthalpy= 0.174548
Thermal correction to Gibbs Free Energy= 0.110732
Sum of electronic and ZPE= -476.894027
Sum of electronic and thermal Energies= -476.877848
Sum of electronic and thermal Enthalpies= -476.876903
Sum of electronic and thermal Free Energies= -476.940720

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.938 54.006 134.313

C,0,2.3119519558,-1.0678310163,1.1438175581
C,0,3.2595746539,-0.4955513001,0.2946029718
C,0,3.0137744648,0.7452071681,-0.2750341343
C,0,1.8340765867,1.4560464413,0.0029561804
C,0,0.9058595774,0.8889566528,0.8754882816
C,0,1.1339407858,-0.3653769983,1.437618523
C,0,1.5894094139,2.7921754403,-0.6397962513
H,0,2.4923478007,-2.0373372449,1.5939597731
H,0,4.1780695789,-1.0242134344,0.0710904125
H,0,3.743472686,1.1796570861,-0.9504489327
H,0,-0.0214957061,1.4103700631,1.0949319694
H,0,0.3938313763,-0.7990118418,2.1019190504
H,0,0.6678055408,3.2454375343,-0.2761421307
H,0,1.515540271,2.6894497892,-1.7252318993
H,0,2.415203635,3.4760541964,-0.4335486222
N,0,0.6033066316,-1.7392391212,-0.8517826992
O,0,0.878079132,-0.9151886295,-1.5481504066
O,0,0.2208354099,-2.6711890063,-0.3675434193
F,0,-3.8458304912,-0.5965395241,0.2368745085
B,0,-2.7518393751,0.2240322034,0.0704776734
F,0,-2.5887958203,1.0111160547,1.1889303439

F,0,-1.6239478751,-0.5606739833,-0.1171657801
F,0,-2.9328202325,1.0212974705,-1.0385899706

TS NO_2BF_4 PCM ONIOM 2.742_94075
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.281649295723

Zero-point correction= 0.157282 (Hartree/Particle)
Thermal correction to Energy= 0.173358
Thermal correction to Enthalpy= 0.174302
Thermal correction to Gibbs Free Energy= 0.111129
Sum of electronic and ZPE= -476.894598
Sum of electronic and thermal Energies= -476.878522
Sum of electronic and thermal Enthalpies= -476.877578
Sum of electronic and thermal Free Energies= -476.940751

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.784 53.994 132.960

C,0,-2.1758758775,-1.1605793379,1.1659709875
C,0,-1.0036682114,-0.4225299404,1.3900926485
C,0,-0.8454798091,0.8435373145,0.8243591998
C,0,-1.8385385901,1.384336082,0.0111163724
C,0,-3.0089259289,0.6364570947,-0.2001872126
C,0,-3.1849938244,-0.6146508683,0.3763634323
C,0,-1.6752957276,2.7267264907,-0.6444584712
H,0,-2.2985541947,-2.1361610845,1.6219081051
H,0,-0.211501113,-0.8342483285,2.0086050299
H,0,0.0819794638,1.3865097724,0.9896497199
H,0,-3.7891397156,1.04995284,-0.8306392372
H,0,-4.0990257105,-1.1683914424,0.2013396595
H,0,-1.6456284619,2.6213676374,-1.7317241379
H,0,-0.7573414661,3.2178462159,-0.3236922597
H,0,-2.5181584396,3.3774968311,-0.4036317123
N,0,-0.4320162787,-1.6586770531,-0.8911414942
O,0,-0.9201033941,-0.9533677078,-1.6030754113
O,0,0.160840161,-2.4826399997,-0.4198615699
F,0,1.6785127479,-0.0832303557,-0.8760443011
B,0,2.6101072289,0.2807360038,0.0856367947
F,0,3.8635838047,-0.1078006484,-0.3304456661
F,0,2.5797682523,1.6446201609,0.2695127468
F,0,2.2866250845,-0.3641566768,1.2604547769

TS NO_2BF_4 PCM ONIOM 2.776_93985
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.281369632739

Zero-point correction= 0.157929 (Hartree/Particle)
Thermal correction to Energy= 0.173892

Thermal correction to Enthalpy= 0.174836
Thermal correction to Gibbs Free Energy= 0.112232
Sum of electronic and ZPE= -476.894156
Sum of electronic and thermal Energies= -476.878194
Sum of electronic and thermal Enthalpies= -476.877249
Sum of electronic and thermal Free Energies= -476.939853

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.119 53.794 131.760

C,0,-2.1592162888,-1.2691328579,1.0968431457
C,0,-1.0647400636,-0.4548409042,1.4254238728
C,0,-0.9600667674,0.8339133152,0.90252836
C,0,-1.931724389,1.3270626062,0.0323801525
C,0,-3.0262369922,0.505289644,-0.2793599879
C,0,-3.1472747848,-0.7739488307,0.2504821682
C,0,-1.8022711025,2.6893226631,-0.5891385618
H,0,-2.2425900724,-2.2634510131,1.519587532
H,0,-0.2929961084,-0.8277041222,2.092210775
H,0,-0.0936751127,1.441126681,1.1512616263
H,0,-3.7915001786,0.8808657368,-0.9504644224
H,0,-4.0042341865,-1.3860200902,-0.0026815437
H,0,-2.7752052678,3.17325231,-0.6815672184
H,0,-1.3792871148,2.6079344008,-1.5944806738
H,0,-1.1465436485,3.3320372856,-0.0021235174
N,0,-0.2353581887,-1.5673033644,-0.8832901832
O,0,-0.750379684,-0.8741413085,-1.5866986848
O,0,0.3882131071,-2.356687437,-0.397231002
F,0,2.0839242704,-0.5744424092,1.0235325738
B,0,2.5690190161,0.3206601807,0.0904948053
F,0,2.4754403533,1.6057498744,0.572404079
F,0,3.876349794,0.0220457672,-0.2152541088
F,0,1.7837514099,0.1811148724,-1.0434231863

TS NO_2BF_4 PCM ONIOM 2.967_93897
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.286733098719

Zero-point correction= 0.157529 (Hartree/Particle)
Thermal correction to Energy= 0.173441
Thermal correction to Enthalpy= 0.174385
Thermal correction to Gibbs Free Energy= 0.112496
Sum of electronic and ZPE= -476.893942
Sum of electronic and thermal Energies= -476.878030
Sum of electronic and thermal Enthalpies= -476.877086
Sum of electronic and thermal Free Energies= -476.938974

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K

Total 108.836 53.968 130.255

C,0,0.5150953323,1.3864896702,0.5293945678
C,0,0.9150109798,0.3146227384,1.3312595361
C,0,2.1716666343,-0.2921581852,1.1422732745
C,0,3.0321170754,0.1514104175,0.1417984112
C,0,2.6001162069,1.2043081384,-0.6721943744
C,0,1.3609377491,1.8197301208,-0.4823093835
C,0,4.3803656685,-0.4783994172,-0.0768821301
H,0,-0.461218166,1.8382681677,0.6749470812
H,0,0.2584363433,-0.0442841529,2.1179149498
H,0,2.4708265221,-1.107663799,1.7921439811
H,0,3.2474870895,1.5525823865,-1.4703359001
H,0,1.0606404219,2.6324605526,-1.1321854404
H,0,5.1723197943,0.2623806827,0.0491047078
H,0,4.4638432378,-0.8769383567,-1.090056717
H,0,4.5581142136,-1.2898977019,0.6279722
N,0,0.2567097919,-1.3998875899,-0.4586812227
O,0,0.6532860251,-0.929133621,-1.3933778436
O,0,-0.2547338205,-2.1184359992,0.2360694752
F,0,-2.0450437022,-0.1703730071,-1.1002249315
B,0,-2.8339244033,0.1696770229,-0.0120586857
F,0,-4.0556286177,-0.4539421713,-0.1130910553
F,0,-2.1696181306,-0.2732395659,1.1154112349
F,0,-3.0003012455,1.5340456693,0.0400682647

TS NO_2BF_4 PCM ONIOM 2.998_94196 (**6a‡**)
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.285542011062

Zero-point correction= 0.157344 (Hartree/Particle)
Thermal correction to Energy= 0.173485
Thermal correction to Enthalpy= 0.174429
Thermal correction to Gibbs Free Energy= 0.109301
Sum of electronic and ZPE= -476.893257
Sum of electronic and thermal Energies= -476.877116
Sum of electronic and thermal Enthalpies= -476.876172
Sum of electronic and thermal Free Energies= -476.941300

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.863 53.951 137.074

C,0,0.3947296521,-1.1883715728,0.6862498997
C,0,1.1040211645,-1.7910502132,-0.3440539161
C,0,2.4065960889,-1.3801134014,-0.6409877201
C,0,3.0368291717,-0.3627020573,0.0798424992
C,0,2.3083297344,0.2610990745,1.0920428013
C,0,0.9921223037,-0.144354218,1.3929849978
C,0,4.4496317367,0.0439271191,-0.2376442475

H,0,-0.6259904464,-1.4859349479,0.9081100116
H,0,0.6470993888,-2.5814317025,-0.9272966141
H,0,2.9423011255,-1.8646935455,-1.4507270029
H,0,2.7618781328,1.0591778526,1.6710342903
H,0,0.4544898883,0.3482034576,2.1960341571
H,0,5.1382466032,-0.7757707321,-0.0227544029
H,0,4.7565250617,0.907269529,0.3522041183
H,0,4.5565695618,0.2924298118,-1.2952358331
N,0,0.5713564188,1.5858066627,-0.4372626633
O,0,0.716085983,0.9861807251,-1.371218658
O,0,0.3088265442,2.4378858596,0.2468897907
F,0,-3.0694977601,-0.5760204515,1.2779384867
B,0,-2.954745117,-0.1764248109,-0.0352918729
F,0,-2.7376305123,-1.2724252236,-0.8412449412
F,0,-4.1072111267,0.4663268963,-0.4304621832
F,0,-1.8864165977,0.6999918882,-0.1584209976

TS NO_2BF_4 PCM ONIOM 3.076_93756
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.285711715731

Zero-point correction= 0.158386 (Hartree/Particle)
Thermal correction to Energy= 0.173688
Thermal correction to Enthalpy= 0.174633
Thermal correction to Gibbs Free Energy= 0.114875
Sum of electronic and ZPE= -476.894053
Sum of electronic and thermal Energies= -476.878750
Sum of electronic and thermal Enthalpies= -476.877806
Sum of electronic and thermal Free Energies= -476.937563

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.991 53.385 125.770

C,0,-3.2547581362,-0.6243801209,0.3870708919
C,0,-2.1705069763,-0.6130023114,1.2651373096
C,0,-1.183492014,0.3822556807,1.1604210931
C,0,-1.2618157108,1.379338248,0.1803338293
C,0,-2.3346118501,1.3290216903,-0.7074760857
C,0,-3.3218475058,0.3405602225,-0.6064224011
C,0,-0.2109138543,2.4496910932,0.1007971388
H,0,-4.0214984837,-1.3833562729,0.4753522742
H,0,-2.0933817816,-1.3599635944,2.0474379093
H,0,-0.3502279043,0.3837170879,1.8592900893
H,0,-2.4110520295,2.0741178498,-1.4918926883
H,0,-4.1435904222,0.3364673427,-1.31225482
H,0,-0.2289312769,3.0655663939,1.0023267477
H,0,-0.3731445985,3.1010088961,-0.7567849371
H,0,0.807218023,2.0169905486,0.0233614652
N,0,-0.4656414518,-1.6250596029,-0.4423968186

O,0,-0.8558205681,-1.1824418475,-1.3919697122
O,0,0.0730068675,-2.2825523226,0.2892455239
F,0,1.9891051138,-0.4175918161,1.1360055462
B,0,2.5716178752,0.0796740249,-0.0125017901
F,0,2.5123649356,1.4572321756,-0.0067490859
F,0,3.8752202029,-0.3446573073,-0.1082981308
F,0,1.8351885461,-0.406081058,-1.0813093488

TS NO_2BF_4 PCM ONIOM 3.092_93919
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.284342827126

Zero-point correction= 0.157445 (Hartree/Particle)
Thermal correction to Energy= 0.173463
Thermal correction to Enthalpy= 0.174407
Thermal correction to Gibbs Free Energy= 0.111649
Sum of electronic and ZPE= -476.893404
Sum of electronic and thermal Energies= -476.877387
Sum of electronic and thermal Enthalpies= -476.876442
Sum of electronic and thermal Free Energies= -476.939200

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.849 53.908 132.084

C,0,-0.3795939688,-1.4128422029,0.286873647
C,0,-0.7152745902,-0.3940532377,1.1745072438
C,0,-2.0064182075,0.1686041654,1.1561314904
C,0,-2.9764871084,-0.2854556067,0.2575536827
C,0,-2.610720037,-1.2867892962,-0.6409069363
C,0,-1.3287022079,-1.8443143649,-0.6313826168
C,0,-4.3561222921,0.3133778652,0.2299328849
H,0,0.6239628991,-1.8269392216,0.2929014336
H,0,0.0236483572,-0.0305342689,1.8827228224
H,0,-2.25697092,0.9482536844,1.8686563984
H,0,-3.3383645882,-1.6435330999,-1.362189019
H,0,-1.0792811721,-2.6192711861,-1.3462091543
H,0,-5.1123812431,-0.4595754217,0.0897150093
H,0,-4.4520186253,1.0201508931,-0.598338607
H,0,-4.5749722658,0.8468561712,1.154456599
N,0,-0.5800444188,1.5573616385,-0.5512308751
O,0,-0.8265071674,0.9985121712,-1.4875727226
O,0,-0.2381864625,2.3606992115,0.1541117855
F,0,2.6634010048,-0.3570590805,1.3798020907
B,0,2.9065303573,-0.1415516925,0.0409134836
F,0,3.037714,-1.3455968099,-0.6152553628
F,0,1.8455491821,0.5660898923,-0.5055932651
F,0,4.0590884745,0.5975667968,-0.1095530123

TS NO_2BF_4 PCM ONIOM 3.093_93956

ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.284309011817

Zero-point correction= 0.157296 (Hartree/Particle)
Thermal correction to Energy= 0.173338
Thermal correction to Enthalpy= 0.174282
Thermal correction to Gibbs Free Energy= 0.111305
Sum of electronic and ZPE= -476.893601
Sum of electronic and thermal Energies= -476.877560
Sum of electronic and thermal Enthalpies= -476.876616
Sum of electronic and thermal Free Energies= -476.939593

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	108.771	53.938	132.546

C,0,-0.3832312917,-1.4105449184,0.2744952036
C,0,-0.7133255809,-0.3904961179,1.1627920811
C,0,-2.0012939002,0.1786873449,1.1449605429
C,0,-2.9764551172,-0.2737788828,0.2501982099
C,0,-2.6142390738,-1.271608824,-0.653117491
C,0,-1.3341408289,-1.8344503537,-0.6452025729
C,0,-4.3704610904,0.2901643285,0.2683835113
H,0,0.6193531522,-1.8270278056,0.2772592881
H,0,0.0291661311,-0.0269229174,1.8673326189
H,0,-2.2458815012,0.9633770474,1.8540607132
H,0,-3.3413221987,-1.6203657171,-1.378764421
H,0,-1.0868702215,-2.6051440893,-1.3654056931
H,0,-5.0281704068,-0.3565670774,0.8540934602
H,0,-4.7834977232,0.3558582171,-0.7386348114
H,0,-4.3936948923,1.2818451073,0.7204896141
N,0,-0.5751533764,1.5615209707,-0.5631707861
O,0,-0.8130065843,1.0000538006,-1.500150192
O,0,-0.238558675,2.3674095238,0.1420195206
F,0,2.6586765388,-0.3710460261,1.3858832886
B,0,2.9075173277,-0.1465133455,0.0495287922
F,0,3.040921174,-1.3461165369,-0.6142942914
F,0,1.8494395781,0.5652103173,-0.4973702448
F,0,4.0612595605,0.5928329545,-0.0904983411

TS NO_2BF_4 PCM ONIOM 3.099_93450
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.280523634869

Zero-point correction= 0.157616 (Hartree/Particle)
Thermal correction to Energy= 0.173566
Thermal correction to Enthalpy= 0.174510
Thermal correction to Gibbs Free Energy= 0.111767
Sum of electronic and ZPE= -476.888642
Sum of electronic and thermal Energies= -476.872693

Sum of electronic and thermal Enthalpies= -476.871749
Sum of electronic and thermal Free Energies= -476.934492

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.914 53.904 132.055

C,0,-3.7681847838,-0.1030048406,-0.3098101657
C,0,-3.5359779163,0.8542355079,0.6677436454
C,0,-2.3207823696,1.5500349973,0.7132864373
C,0,-1.3103497574,1.3051413901,-0.2115702732
C,0,-1.5339878119,0.3040930866,-1.1678227678
C,0,-2.7566846225,-0.3899381435,-1.2236599099
C,0,-0.01794227,2.0727860165,-0.2025933301
H,0,-4.7120525223,-0.6312239421,-0.3543214266
H,0,-4.3010440225,1.0726827111,1.4033418995
H,0,-2.168857994,2.2993440945,1.4827204439
H,0,-0.7640581473,0.0864973646,-1.9029222078
H,0,-2.9100798601,-1.1371323689,-1.9945572094
H,0,0.0542158849,2.7006299523,-1.0935170328
H,0,0.8467554937,1.4005444738,-0.207492069
H,0,0.0536847157,2.7176210075,0.6725233632
N,0,-1.2335159649,-1.7348745911,0.4127942417
O,0,-1.55028369,-1.2703593437,1.3800864734
O,0,-0.7962810479,-2.4567910853,-0.3278258066
F,0,3.5641318571,1.306858997,-0.2747360345
B,0,3.2374410406,0.0018281682,0.0259924562
F,0,4.3908393548,-0.7327182984,0.2090092329
F,0,2.4866886022,-0.03926299,1.1839562506
F,0,2.5113818314,-0.5479591639,-1.0115632109

TS NO_2BF_4 PCM ONIOM 3.107_93658
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.280227926471

Zero-point correction= 0.157041 (Hartree/Particle)
Thermal correction to Energy= 0.173317
Thermal correction to Enthalpy= 0.174261
Thermal correction to Gibbs Free Energy= 0.109510
Sum of electronic and ZPE= -476.889055
Sum of electronic and thermal Energies= -476.872780
Sum of electronic and thermal Enthalpies= -476.871836
Sum of electronic and thermal Free Energies= -476.936587

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.758 54.046 136.280

C,0,-0.2478575519,-1.063655345,-0.0783260366
C,0,-1.1334577255,-1.6805471471,0.7954031736

C,0,-2.512691603,-1.4687107564,0.680769267
C,0,-3.0404607341,-0.6386917455,-0.3041463934
C,0,-2.1393217414,0.014786356,-1.1545178678
C,0,-0.7516049734,-0.2041567798,-1.0502045603
C,0,-4.5243256209,-0.4511421198,-0.4591840538
H,0,0.8240186074,-1.2217578758,0.0053728004
H,0,-0.7584947342,-2.3341935239,1.574015726
H,0,-3.1837805033,-1.9647328726,1.3736836748
H,0,-2.5167744919,0.6744757399,-1.9299117267
H,0,-0.0735773334,0.297529259,-1.7336007378
H,0,-5.0429934722,-0.6092335389,0.4863487763
H,0,-4.9196100954,-1.1705103562,-1.1805629795
H,0,-4.7635333244,0.5475369468,-0.8261515489
N,0,-1.3359857955,1.7825479794,0.5300425108
O,0,-1.4521504821,1.2200019329,1.4908635209
O,0,-1.193563156,2.6338670075,-0.1896156183
F,0,3.3462878065,-1.3106915217,-0.7483193231
B,0,3.3414289906,-0.1149126975,-0.0606677133
F,0,4.6175755966,0.4082195215,-0.0354166846
F,0,2.4988386103,0.779287158,-0.6902751322
F,0,2.9087887271,-0.3214096208,1.2335289265

TS NO_2BF_4 PCM ONIOM 3.119_93855
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.283232372106

Zero-point correction= 0.158157 (Hartree/Particle)
Thermal correction to Energy= 0.173706
Thermal correction to Enthalpy= 0.174650
Thermal correction to Gibbs Free Energy= 0.113100
Sum of electronic and ZPE= -476.893479
Sum of electronic and thermal Energies= -476.877931
Sum of electronic and thermal Enthalpies= -476.876987
Sum of electronic and thermal Free Energies= -476.938536

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	109.002	53.516	129.542

C,0,3.4948409159,0.2701610057,-0.2827532036
C,0,2.8168147608,0.4945654408,0.9115465642
C,0,1.7035879115,-0.296875606,1.2547915087
C,0,1.2646266756,-1.3294766482,0.4183103945
C,0,1.9413748645,-1.5174136267,-0.7868653265
C,0,3.0412986384,-0.7287940504,-1.1361102332
C,0,0.0766743639,-2.1727473908,0.7792766376
H,0,4.3564224429,0.8709788386,-0.544812752
H,0,3.1535844776,1.2658475952,1.5953276172
H,0,1.1996651773,-0.1235251859,2.2008487915
H,0,1.6092079035,-2.2963201574,-1.4651131297

H,0,3.5447755877,-0.9051984177,-2.0790494532
H,0,-0.1064937723,-2.1598705204,1.8533344998
H,0,0.2238598019,-3.2067198591,0.4667408471
H,0,-0.839736399,-1.8025090133,0.2732519466
N,0,0.7310765548,1.708395222,-0.1370565899
O,0,0.7524128189,1.2425874241,-1.152383538
O,0,0.5242732296,2.4036457241,0.7183641595
F,0,-1.7108360574,0.7768957335,0.1766128492
B,0,-2.8003103231,-0.0286700252,-0.1170053868
F,0,-2.3426783943,-1.2648971012,-0.5281743491
F,0,-3.5808230947,-0.1708358061,1.007847343
F,0,-3.5336840839,0.5543994247,-1.1260911969
TS NO_2BF_4 PCM ONIOM 3.119_93935
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.284974969347

Zero-point correction= 0.157584 (Hartree/Particle)
Thermal correction to Energy= 0.173458
Thermal correction to Enthalpy= 0.174402
Thermal correction to Gibbs Free Energy= 0.112713
Sum of electronic and ZPE= -476.894480
Sum of electronic and thermal Energies= -476.878606
Sum of electronic and thermal Enthalpies= -476.877662
Sum of electronic and thermal Free Energies= -476.939352

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	108.847	53.944	129.837

C,0,-3.3021454725,-0.7248114187,0.3588455249
C,0,-2.2380908749,-0.6681815587,1.257912484
C,0,-1.2938527201,0.3680635734,1.1704369387
C,0,-1.3972857567,1.3623313538,0.1889140065
C,0,-2.4522118164,1.2725529258,-0.7154266065
C,0,-3.3951288085,0.2404835947,-0.6335208041
C,0,-0.3754934517,2.4636173572,0.1206900624
H,0,-4.035539406,-1.5179544007,0.4289189923
H,0,-2.1422389875,-1.4134856101,2.0397750139
H,0,-0.4735149614,0.4055635043,1.8837804999
H,0,-2.54736967,2.0163221534,-1.4989749988
H,0,-4.2037064779,0.2008332721,-1.3535157121
H,0,-0.5672062101,3.1334985279,-0.7162438163
H,0,0.6330803907,2.0506643086,0.006979562
H,0,-0.3829712247,3.0513469474,1.0406753392
N,0,-0.4019599373,-1.5563306484,-0.4324882499
O,0,-0.8435892795,-1.1698838553,-1.3830492586
O,0,0.1925975886,-2.1429020321,0.3143236405
F,0,3.1474863882,1.3811552349,-0.0923456203
B,0,2.658438859,0.0981847026,-0.0160883511
F,0,1.7852748263,-0.149863002,-1.0645781328

F,0,3.6961063469,-0.8046349996,-0.069412343
F,0,1.9459236553,-0.0829949306,1.1527528292

TS NO_2BF_4 PCM ONIOM 3.125_93949
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.283497076933

Zero-point correction= 0.157586 (Hartree/Particle)
Thermal correction to Energy= 0.173581
Thermal correction to Enthalpy= 0.174525
Thermal correction to Gibbs Free Energy= 0.111589
Sum of electronic and ZPE= -476.893496
Sum of electronic and thermal Energies= -476.877502
Sum of electronic and thermal Enthalpies= -476.876558
Sum of electronic and thermal Free Energies= -476.939494

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.924 53.955 132.460

C,0,-3.5106872231,-0.3059477972,-0.3260345591
C,0,-2.8598944005,-0.5149651651,0.8863693476
C,0,-1.7656462627,0.2919453025,1.2506518874
C,0,-1.319812659,1.327060102,0.4193817859
C,0,-1.9672922366,1.499557085,-0.8022911633
C,0,-3.0477575726,0.6925382385,-1.1741939158
C,0,-0.1561875222,2.1919525353,0.8177615518
H,0,-4.3581301776,-0.9188690051,-0.6057240094
H,0,-3.2034101843,-1.2857176176,1.5674493486
H,0,-1.2823178495,0.1302331014,2.2097442285
H,0,-1.6302523757,2.2795360548,-1.4766784715
H,0,-3.5292875776,0.8564537443,-2.1309054025
H,0,-0.1042226303,2.3080327568,1.9004866524
H,0,-0.2316182332,3.1808203727,0.3658234538
H,0,0.7901922845,1.7482821864,0.4851063744
N,0,-0.7171387762,-1.6907998611,-0.103671641
O,0,-0.4878031396,-2.3592822083,0.7675538645
O,0,-0.7545418245,-1.2520213936,-1.1306987941
F,0,3.8423083218,-0.8456937962,-0.4570604309
B,0,2.8395065915,0.0385420048,-0.1240468969
F,0,2.5848577758,0.8684671106,-1.1940631054
F,0,1.6924331952,-0.6788945848,0.1817192364
F,0,3.2219694763,0.7831488338,0.9697266588

TS NO_2BF_4 PCM ONIOM 3.130_93945
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.283803815230

Zero-point correction= 0.157378 (Hartree/Particle)
Thermal correction to Energy= 0.173421

Thermal correction to Enthalpy= 0.174365
Thermal correction to Gibbs Free Energy= 0.111440
Sum of electronic and ZPE= -476.893528
Sum of electronic and thermal Energies= -476.877484
Sum of electronic and thermal Enthalpies= -476.876540
Sum of electronic and thermal Free Energies= -476.939465

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.823 53.937 132.437

C,0,-0.3827288153,-1.4610221546,0.1860600006
C,0,-0.6513585541,-0.4550868045,1.1088562922
C,0,-1.9239847498,0.1455550433,1.1531613278
C,0,-2.9482795031,-0.2675261064,0.2925640323
C,0,-2.6495167988,-1.256817626,-0.6416041543
C,0,-1.3830608543,-1.8469487593,-0.6985263663
C,0,-4.3253387828,0.3305942357,0.3801615901
H,0,0.6096287635,-1.8981210547,0.1368708035
H,0,0.1287841251,-0.1200936112,1.7866270022
H,0,-2.1204096856,0.920030997,1.8882922977
H,0,-3.4151456216,-1.5764082995,-1.3404266038
H,0,-1.1850234924,-2.6093653903,-1.442478374
H,0,-4.3022813081,1.3172879667,0.8432682057
H,0,-4.972229746,-0.3060910697,0.9884778382
H,0,-4.7812831559,0.4189436895,-0.6064310288
N,0,-0.617653682,1.560350888,-0.5984585371
O,0,-0.820713415,0.9756908177,-1.5291548209
O,0,-0.3193111032,2.3866609268,0.0997403972
F,0,2.7209804267,-0.4954340705,1.3831726791
B,0,2.9074428062,-0.1298280611,0.0681636818
F,0,3.008173531,-1.2539936698,-0.7219384011
F,0,1.8291347589,0.6335817597,-0.3547038125
F,0,4.0567338565,0.6210913532,-0.0462400498

TS NO_2BF_4 PCM ONIOM 3.138_94010
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.280523313130

Zero-point correction= 0.156402 (Hartree/Particle)
Thermal correction to Energy= 0.173090
Thermal correction to Enthalpy= 0.174034
Thermal correction to Gibbs Free Energy= 0.104549
Sum of electronic and ZPE= -476.888255
Sum of electronic and thermal Energies= -476.871567
Sum of electronic and thermal Enthalpies= -476.870623
Sum of electronic and thermal Free Energies= -476.940108

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K

Total 108.616 54.288 146.245

C,0,-2.95621,-1.965957,0.224333
C,0,-2.943216,-1.029008,1.250913
C,0,-3.250011,0.320777,0.980886
C,0,-3.602886,0.742775,-0.308982
C,0,-3.574924,-0.205569,-1.326573
C,0,-3.253709,-1.543082,-1.066063
C,0,-4.001371,2.167369,-0.575858
H,0,-2.720651,-3.0035,0.425229
H,0,-2.70719,-1.327685,2.266471
H,0,-3.256643,1.036737,1.797443
H,0,-3.809304,0.095037,-2.342362
H,0,-3.241616,-2.254206,-1.883756
H,0,-5.088353,2.267056,-0.521953
H,0,-3.68933,2.48585,-1.570782
H,0,-3.570825,2.847353,0.159722
N,0,-0.743892,0.229963,0.588546
O,0,-0.692354,-0.083251,-0.486151
O,0,-0.414449,0.607074,1.596045
F,0,3.533152,0.65596,-0.938277
B,0,4.480576,0.027604,-0.15624
F,0,5.278164,-0.768239,-0.951292
F,0,5.255887,0.976531,0.476423
F,0,3.847983,-0.754118,0.788731

TS NO_2BF_4 PCM ONIOM 3.139_93772
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.280226078977

Zero-point correction= 0.157220 (Hartree/Particle)
Thermal correction to Energy= 0.173691
Thermal correction to Enthalpy= 0.174635
Thermal correction to Gibbs Free Energy= 0.107388
Sum of electronic and ZPE= -476.887891
Sum of electronic and thermal Energies= -476.871420
Sum of electronic and thermal Enthalpies= -476.870476
Sum of electronic and thermal Free Energies= -476.937723

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.993 54.093 141.534

C,0,-1.319303,1.607591,0.685691
C,0,-2.102119,1.954466,-0.409645
C,0,-3.237448,1.20703,-0.743209
C,0,-3.617479,0.095922,0.004192
C,0,-2.795213,-0.278644,1.075673
C,0,-1.659132,0.479431,1.424391
C,0,-4.869053,-0.672238,-0.318656

H,0,-0.447581,2.193537,0.949457
H,0,-1.835655,2.81467,-1.012676
H,0,-3.834149,1.502269,-1.599815
H,0,-3.060504,-1.143505,1.676582
H,0,-1.06128,0.181569,2.279062
H,0,-5.059757,-0.684678,-1.392082
H,0,-5.729473,-0.20302,0.164834
H,0,-4.80983,-1.700581,0.038273
N,0,-0.950084,-1.3368,-0.337819
O,0,-0.979226,-0.691052,-1.252005
O,0,-0.706508,-2.194339,0.346731
F,0,4.925431,-0.482174,0.803191
B,0,3.991965,0.076864,-0.044034
F,0,2.986034,0.658574,0.700477
F,0,4.593989,1.03433,-0.832925
F,0,3.451585,-0.906862,-0.847096

TS NO_2BF_4 PCM ONIOM 3.146_93865
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.279983587293

Zero-point correction= 0.156982 (Hartree/Particle)
Thermal correction to Energy= 0.173553
Thermal correction to Enthalpy= 0.174497
Thermal correction to Gibbs Free Energy= 0.106381
Sum of electronic and ZPE= -476.888056
Sum of electronic and thermal Energies= -476.871486
Sum of electronic and thermal Enthalpies= -476.870542
Sum of electronic and thermal Free Energies= -476.938658

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.906 54.128 143.362

C,0,-1.568092,1.776682,0.451435
C,0,-2.54018,1.93872,-0.528878
C,0,-3.580674,1.012298,-0.665832
C,0,-3.674246,-0.098298,0.166994
C,0,-2.663083,-0.28221,1.121047
C,0,-1.623068,0.656115,1.27353
C,0,-4.817839,-1.068314,0.057302
H,0,-0.771132,2.501018,0.564292
H,0,-2.498975,2.793312,-1.193979
H,0,-4.32981,1.166667,-1.43505
H,0,-2.704812,-1.141087,1.78422
H,0,-0.872954,0.500807,2.041573
H,0,-4.518785,-2.072476,0.359428
H,0,-5.204596,-1.111201,-0.960952
H,0,-5.636573,-0.757078,0.710765
N,0,-0.884306,-1.146529,-0.49187

O,0,-1.135551,-0.575225,-1.421562
O,0,-0.42251,-1.911287,0.190056
F,0,4.877063,1.017677,-0.611263
B,0,4.099137,0.059828,0.004276
F,0,3.478706,-0.71494,-0.954507
F,0,4.891964,-0.741487,0.798668
F,0,3.141121,0.675277,0.783754

TS NO_2BF_4 PCM ONIOM 3.182_93693
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.283532272052

Zero-point correction= 0.157814 (Hartree/Particle)
Thermal correction to Energy= 0.173702
Thermal correction to Enthalpy= 0.174647
Thermal correction to Gibbs Free Energy= 0.112236
Sum of electronic and ZPE= -476.891358
Sum of electronic and thermal Energies= -476.875469
Sum of electronic and thermal Enthalpies= -476.874525
Sum of electronic and thermal Free Energies= -476.936936

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.000 53.827 131.355

C,0,0.869728,1.840317,-0.086325
C,0,2.051368,1.859372,0.646381
C,0,3.015822,0.861411,0.471833
C,0,2.821829,-0.179212,-0.431552
C,0,1.610064,-0.214012,-1.136783
C,0,0.645044,0.796086,-0.977356
C,0,3.873244,-1.229633,-0.662165
H,0,0.11815,2.607175,0.054118
H,0,2.22952,2.652118,1.363059
H,0,3.930564,0.899372,1.052942
H,0,1.42673,-1.018669,-1.842448
H,0,-0.28859,0.742605,-1.532729
H,0,4.470107,-0.974814,-1.541352
H,0,3.425287,-2.207942,-0.842251
H,0,4.549518,-1.306874,0.188886
N,0,0.19155,-1.119438,0.868088
O,0,-0.411148,-1.843825,0.263601
O,0,0.655733,-0.56242,1.720992
F,0,-2.143484,-1.045484,-0.649591
B,0,-2.760882,0.087827,-0.148865
F,0,-1.928274,0.573804,0.847119
F,0,-2.907,1.025727,-1.143805
F,0,-3.985352,-0.237608,0.384782

TS NO_2BF_4 PCM ONIOM 3.341_93662

ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.281527933861

Zero-point correction= 0.157834 (Hartree/Particle)
Thermal correction to Energy= 0.173687
Thermal correction to Enthalpy= 0.174631
Thermal correction to Gibbs Free Energy= 0.112712
Sum of electronic and ZPE= -476.891431
Sum of electronic and thermal Energies= -476.875578
Sum of electronic and thermal Enthalpies= -476.874634
Sum of electronic and thermal Free Energies= -476.936553

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.990 53.810 130.318

C,0,1.1925142962,2.0209814205,-0.0626052304
C,0,2.4179528437,1.7784993049,0.5580469855
C,0,3.1166354993,0.5956471237,0.3194253928
C,0,2.6053642051,-0.3778583479,-0.5359148493
C,0,1.3568263337,-0.135020221,-1.1353614835
C,0,0.6624017372,1.0619857621,-0.915252695
C,0,3.3703558879,-1.6374970087,-0.8354166172
H,0,0.6548625998,2.9409276166,0.1293491737
H,0,2.8328447913,2.51575558,1.2351412447
H,0,4.0696525594,0.4285809059,0.8090472676
H,0,0.9300012401,-0.8822024324,-1.7986317292
H,0,-0.305730639,1.214178878,-1.3852122752
H,0,4.0011298506,-1.4906021477,-1.7158175371
H,0,2.7002012488,-2.4714129538,-1.0493196199
H,0,4.0191059872,-1.9141237035,-0.004296111
N,0,0.1906914861,-0.9559005745,1.0780010733
O,0,-0.3635076842,-1.7751955651,0.5587049054
O,0,0.6187281238,-0.2470038306,1.8273412336
F,0,-1.9512120614,-0.986894728,-0.6451485094
B,0,-2.7155832503,0.072259934,-0.1848121496
F,0,-2.0019267598,0.6322853106,0.8632245527
F,0,-2.8987501667,0.9982631414,-1.1843998396
F,0,-3.9300651287,-0.3848564646,0.2686428171

Pi Complexes for Toluene / $NO_2^+BF_4^-$ ONIOM(M062X/6-311G*:PM3)/PCM(CH_2Cl_2)
*Pi Complex NO_2BF_4 PCM ONIOM 2.727_94123*ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.277319186051

Zero-point correction= 0.157909 (Hartree/Particle)
Thermal correction to Energy= 0.174806
Thermal correction to Enthalpy= 0.175751
Thermal correction to Gibbs Free Energy= 0.110238
Sum of electronic and ZPE= -476.893568
Sum of electronic and thermal Energies= -476.876670

Sum of electronic and thermal Enthalpies= -476.875726
Sum of electronic and thermal Free Energies= -476.941238

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.693 55.813 137.883

C,0,2.0243110462,-1.1198338361,-1.2361097836
C,0,0.9237187983,-0.261719388,-1.3653063835
C,0,0.9343670649,0.9870599447,-0.7503421204
C,0,2.0317817943,1.3987786419,0.0084284194
C,0,3.1324000593,0.535138849,0.117631817
C,0,3.1367467403,-0.7068679903,-0.5015778393
C,0,2.0351339021,2.7245979483,0.7162011028
H,0,2.0200468404,-2.0865279526,-1.7266708772
H,0,0.0556473451,-0.5721357543,-1.9381463024
H,0,0.0651546775,1.6323434211,-0.8400670706
H,0,3.9934542015,0.8489090961,0.6983134749
H,0,3.9984873981,-1.3568468226,-0.4110019521
H,0,1.8207997292,2.5885718158,1.7798688004
H,0,1.2815676458,3.3963897177,0.3057825866
H,0,3.0106355006,3.2068111431,0.6381683703
N,0,0.5464302646,-1.6808939886,0.9866215372
O,0,0.9318424854,-0.8588596325,1.6283541808
O,0,0.0784531361,-2.5902563669,0.5401311422
F,0,-2.5076498748,1.5285181873,-0.5064847311
B,0,-2.7743416203,0.2314361905,-0.1283938447
F,0,-3.1826965483,-0.5004014606,-1.2218708245
F,0,-1.6297273853,-0.3467885189,0.3998629116
F,0,-3.7623212012,0.222309756,0.8321183862

Pi Complex NO_2BF_4 PCM ONIOM 2.731_94156
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.275835792227

Zero-point correction= 0.158085 (Hartree/Particle)
Thermal correction to Energy= 0.174956
Thermal correction to Enthalpy= 0.175900
Thermal correction to Gibbs Free Energy= 0.109954
Sum of electronic and ZPE= -476.893430
Sum of electronic and thermal Energies= -476.876559
Sum of electronic and thermal Enthalpies= -476.875615
Sum of electronic and thermal Free Energies= -476.941561

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.786 55.764 138.795

C,0,-2.7526799987,-3.2822077645,-0.5237856215
C,0,-3.7168170082,-2.9617021087,-1.4871374555

C,0,-3.4138564705,-3.0727555219,-2.8409388706
C,0,-2.1492491674,-3.492992918,-3.257407313
C,0,-1.1936607732,-3.814752487,-2.2818607745
C,0,-1.4903509322,-3.7224208487,-0.929035911
C,0,-1.800914383,-3.5972160511,-4.7159635405
H,0,-2.9913243822,-3.2077210482,0.5314188011
H,0,-4.7051315343,-2.6419946115,-1.1768870659
H,0,-4.1663230025,-2.8261091741,-3.5818076776
H,0,-0.2073445043,-4.141366856,-2.5948114047
H,0,-0.7362163279,-3.9638440473,-0.1862393024
H,0,-2.6749267096,-3.4374056538,-5.3465884272
H,0,-1.38563567,-4.5808317214,-4.9438433899
H,0,-1.0448351507,-2.8555731293,-4.9856037385
N,0,-2.0685680996,-0.6836914865,-1.0168195253
O,0,-2.5553819302,-0.3191541654,-0.0826821915
O,0,-1.5233869155,-0.8511953567,-1.9700062745
F,0,1.3794214955,-0.9445783826,2.105780924
B,0,1.1823587158,-1.7872517893,1.0339931238
F,0,2.2368678065,-1.6754631829,0.1544564462
F,0,1.0805428465,-3.087689755,1.4760644311
F,0,0.0118732954,-1.42627814,0.3837912579

Pi Complex NO_2BF_4 PCM ONIOM 2.750_94123
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.275463893129

Zero-point correction= 0.158040 (Hartree/Particle)
Thermal correction to Energy= 0.174847
Thermal correction to Enthalpy= 0.175791
Thermal correction to Gibbs Free Energy= 0.110262
Sum of electronic and ZPE= -476.893452
Sum of electronic and thermal Energies= -476.876646
Sum of electronic and thermal Enthalpies= -476.875701
Sum of electronic and thermal Free Energies= -476.941230

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.718 55.756 137.917

C,0,-1.3542900963,-0.957284536,1.3924321068
C,0,-0.9517617727,0.3747870075,1.2660824863
C,0,-1.7057838568,1.254239155,0.5010209439
C,0,-2.8831104377,0.8347977899,-0.1356706858
C,0,-3.282975175,-0.4951835944,0.0088757669
C,0,-2.5269544952,-1.388519579,0.7621469735
C,0,-3.6869510619,1.8131561631,-0.9461448302
H,0,-0.7695390938,-1.6495774174,1.9880289592
H,0,-0.0366126111,0.7135481094,1.7421987087
H,0,-1.3824881422,2.2842660478,0.391052719
H,0,-4.1920380861,-0.8361416429,-0.4742170844

H,0,-2.8523426845,-2.4168023538,0.870784776
H,0,-4.5398553098,1.3325527781,-1.423952779
H,0,-3.0707047742,2.2740842225,-1.721335919
H,0,-4.0604732241,2.6179062565,-0.3087173432
N,0,-0.3178322503,-1.5008319031,-1.096176228
O,0,0.167104222,-2.4366465528,-0.7349601101
O,0,-0.7200362836,-0.6105302001,-1.6234512444
F,0,3.1381463412,1.561208126,-0.5900821345
B,0,2.8239116312,0.5576290366,0.2997863688
F,0,3.8956983854,-0.2971772124,0.435127625
F,0,2.5075457227,1.101718914,1.5250915272
F,0,1.7367060527,-0.1547796146,-0.1832936026

Pi Complex NO_2BF_4 PCM ONIOM 2.750_94145
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.276758808342

Zero-point correction= 0.157889 (Hartree/Particle)
Thermal correction to Energy= 0.174751
Thermal correction to Enthalpy= 0.175695
Thermal correction to Gibbs Free Energy= 0.110402
Sum of electronic and ZPE= -476.893966
Sum of electronic and thermal Energies= -476.877105
Sum of electronic and thermal Enthalpies= -476.876161
Sum of electronic and thermal Free Energies= -476.941454

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.658 55.760 137.421

C,0,0.0883681213,-1.5282565367,-0.3839513117
C,0,-1.1443820513,-1.0645989768,-0.8611158729
C,0,-1.2003556734,0.0558516397,-1.686939576
C,0,-0.0365030615,0.7355809432,-2.0467953649
C,0,1.1930285935,0.2542120977,-1.569269543
C,0,1.2600671874,-0.8671268523,-0.7545149194
C,0,-0.0811450378,1.9548302944,-2.9246014497
H,0,0.1316582705,-2.4065105815,0.2498150055
H,0,-2.065350787,-1.5682226883,-0.5809207645
H,0,-2.1691711078,0.4181852941,-2.0219845939
H,0,2.1054727793,0.773291037,-1.8440457486
H,0,2.2193339695,-1.2250730886,-0.4007372123
H,0,-1.1045114703,2.2116338672,-3.1967034003
H,0,0.485100401,1.7859837355,-3.8431536072
H,0,0.3669349051,2.8134465043,-2.4196051155
N,0,-0.6413911065,0.3900824665,1.4463390135
O,0,-0.2191888005,1.2594192574,0.8979017559
O,0,-1.0710499946,-0.3454775614,2.1662488367
F,0,-3.0831652049,0.8922532035,0.6330929634
B,0,-4.2812859844,0.8313023519,-0.0642206828

F,0,-5.3144993488,1.1132538618,0.8023390884
F,0,-4.2630811234,1.75889895,-1.0824156464
F,0,-4.4452247756,-0.4344443184,-0.5824140543

Pi Complex NO_2BF_4 PCM ONIOM 2.754_94188
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.275832663268

Zero-point correction= 0.157975 (Hartree/Particle)
Thermal correction to Energy= 0.174817
Thermal correction to Enthalpy= 0.175762
Thermal correction to Gibbs Free Energy= 0.109972
Sum of electronic and ZPE= -476.893882
Sum of electronic and thermal Energies= -476.877039
Sum of electronic and thermal Enthalpies= -476.876095
Sum of electronic and thermal Free Energies= -476.941885

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.700 55.768 138.467

C,0,0.6484210141,0.0548256445,1.4246063295
C,0,0.576774373,-1.0858450623,0.6265568603
C,0,1.6763817423,-1.4720778693,-0.1309907103
C,0,2.8733311266,-0.7444165712,-0.0928279513
C,0,2.9397932494,0.3883728763,0.7218994546
C,0,1.8391825742,0.7927034487,1.4712657631
C,0,4.068728052,-1.1913893963,-0.8879386482
H,0,-0.2179645712,0.3658310946,2.0009667594
H,0,-0.3527793388,-1.6460085456,0.5731282287
H,0,1.609877126,-2.3495700526,-0.7652356576
H,0,3.8590679097,0.9621420723,0.7653337297
H,0,1.9053133145,1.673540542,2.1000926967
H,0,4.691141829,-1.8579397226,-0.2849470145
H,0,4.6866526395,-0.3438595285,-1.1860561599
H,0,3.7702908737,-1.7381915779,-1.7827462759
N,0,0.3737714708,1.7637747488,-0.7175227834
O,0,0.857157424,1.0910607023,-1.4571226283
O,0,-0.1552223856,2.552679057,-0.1350064751
F,0,-2.6990885913,-0.4454847688,1.3163937799
B,0,-2.8393762995,-0.4272221369,-0.053936167
F,0,-2.7485555596,-1.7069878791,-0.5553045257
F,0,-4.0604636975,0.1160946627,-0.3879552552
F,0,-1.8351032751,0.354018262,-0.6073163494

Pi Complex NO_2BF_4 PCM ONIOM 2.763_94064
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.274782288346

Zero-point correction= 0.158015 (Hartree/Particle)

Thermal correction to Energy= 0.174810
Thermal correction to Enthalpy= 0.175754
Thermal correction to Gibbs Free Energy= 0.110746
Sum of electronic and ZPE= -476.893373
Sum of electronic and thermal Energies= -476.876578
Sum of electronic and thermal Enthalpies= -476.875634
Sum of electronic and thermal Free Energies= -476.940641

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.695 55.730 136.820

C,0,-1.3305096692,0.6246798162,1.7183039599
C,0,-2.6215812971,0.9402745364,1.2834924297
C,0,-3.2795795229,0.0986236824,0.3939265035
C,0,-2.6684531357,-1.068096806,-0.0765769715
C,0,-1.3811675004,-1.3806580423,0.3786465806
C,0,-0.7159466804,-0.5483719149,1.2699805992
C,0,-3.3599159245,-1.9576873963,-1.07184155
H,0,-0.8163856445,1.2750953182,2.4171792285
H,0,-3.1101338729,1.8371959221,1.6459543221
H,0,-4.2803464694,0.3478134125,0.0579393665
H,0,-0.8973637382,-2.2847722131,0.0240929822
H,0,0.2881542985,-0.7975628075,1.6004363663
H,0,-4.4348378863,-1.7787520047,-1.0856530589
H,0,-3.184708929,-3.0103355059,-0.8454817307
H,0,-2.9764425028,-1.7713564822,-2.0791625333
N,0,-0.5436955526,1.7728782412,-0.6692212219
O,0,-0.039534421,2.6067366163,-0.1302585548
O,0,-0.9964712766,1.0268228573,-1.3545997299
F,0,2.7838075074,-0.9457494638,0.9670968215
B,0,2.7991020786,-0.3882176067,-0.2921562064
F,0,2.8336708458,-1.3832792828,-1.2441014758
F,0,1.6555908028,0.3749407516,-0.476187582
F,0,3.9037654904,0.423644372,-0.4282355448

Pi Complex NO_2BF_4 PCM ONIOM 2.765_93840
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.269314072713

Zero-point correction= 0.158372 (Hartree/Particle)
Thermal correction to Energy= 0.174965
Thermal correction to Enthalpy= 0.175909
Thermal correction to Gibbs Free Energy= 0.110873
Sum of electronic and ZPE= -476.890907
Sum of electronic and thermal Energies= -476.874314
Sum of electronic and thermal Enthalpies= -476.873370
Sum of electronic and thermal Free Energies= -476.938406

E CV S

KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.792 55.407 136.879

C,0,-1.2151308202,0.6288312051,1.2999564902
C,0,-2.5689066913,0.9632149359,1.1936019162
C,0,-3.4382906609,0.1370886099,0.4865960128
C,0,-2.9742334923,-1.027562861,-0.1274679026
C,0,-1.6154697885,-1.352802616,-0.0067269952
C,0,-0.7403078472,-0.5414274677,0.7031228915
C,0,-3.8986911294,-1.928346949,-0.8991632547
H,0,-0.5410887181,1.265261516,1.8626909118
H,0,-2.9435404288,1.8597042355,1.6744467667
H,0,-4.4869568825,0.4020402826,0.4095246248
H,0,-1.2448601327,-2.25665729,-0.4793980801
H,0,0.3250869279,-0.8128541544,0.7876422834
H,0,-3.526022879,-2.0922918314,-1.9127567513
H,0,-4.9023829195,-1.5095827838,-0.9650371871
H,0,-3.9684007972,-2.9064675259,-0.41772505
N,0,-1.2033431051,1.9352278478,-1.1375795281
O,0,-1.6228771859,1.09969079,-1.7341285314
O,0,-0.760601548,2.8520996427,-0.6888388316
F,0,2.6428407548,0.1953583873,-0.6961039669
B,0,3.0867133555,-0.521987459,0.3953436374
F,0,3.568359213,0.3475818259,1.3504690871
F,0,2.0345277517,-1.2481104392,0.923478247
F,0,4.0872850237,-1.3850629011,0.0040922101

Pi Complex NO_2BF_4 PCM ONIOM 2.768_94165
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.274298805200

Zero-point correction= 0.157883 (Hartree/Particle)
Thermal correction to Energy= 0.174813
Thermal correction to Enthalpy= 0.175757
Thermal correction to Gibbs Free Energy= 0.109751
Sum of electronic and ZPE= -476.893523
Sum of electronic and thermal Energies= -476.876592
Sum of electronic and thermal Enthalpies= -476.875648
Sum of electronic and thermal Free Energies= -476.941655

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.697 55.769 138.923

C,0,-1.8085554837,2.0886892327,1.6905850152
C,0,-1.9632011711,2.6919178773,0.4376302692
C,0,-2.7137650807,2.0628214832,-0.5454888973
C,0,-3.3341921216,0.8296688184,-0.3021757839
C,0,-3.1863626774,0.2453924064,0.9587109152
C,0,-2.4318357643,0.8655807672,1.9505467575

C,0,-4.1475301839,0.1650088323,-1.3780240051
H,0,-1.2262091833,2.5781167312,2.4633064818
H,0,-1.496294967,3.6488961598,0.23701982
H,0,-2.8245392585,2.5290593649,-1.5191075439
H,0,-3.6577158185,-0.7098227315,1.1629666621
H,0,-2.3128700674,0.3869385904,2.9185854221
H,0,-3.58511137,0.1031015272,-2.3118762822
H,0,-5.0529686703,0.7416634667,-1.5819865746
H,0,-4.4457595479,-0.8418738845,-1.0871773309
N,0,0.1623715847,0.5029685731,0.5665679692
O,0,-0.4483559553,0.072921305,-0.2539745481
O,0,0.910271627,0.854687273,1.3123964218
F,0,-0.3823956847,-1.4319010115,2.2603891697
B,0,-0.5215161356,-2.1917400705,3.4120342712
F,0,0.5093685691,-1.8917354944,4.2754769211
F,0,-1.727756526,-1.9031717334,4.0111301753
F,0,-0.4753605136,-3.5270334831,3.0767858949

Pi Complex NO_2BF_4 PCM ONIOM 2.770_94103
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.269841120227

Zero-point correction= 0.158274 (Hartree/Particle)
Thermal correction to Energy= 0.175059
Thermal correction to Enthalpy= 0.176003
Thermal correction to Gibbs Free Energy= 0.108264
Sum of electronic and ZPE= -476.891026
Sum of electronic and thermal Energies= -476.874242
Sum of electronic and thermal Enthalpies= -476.873297
Sum of electronic and thermal Free Energies= -476.941036

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.851 55.436 142.568

C,0,-2.381805155,-3.6461105929,-0.7101818265
C,0,-3.3944953505,-4.1429224965,-1.5320349979
C,0,-3.2569487544,-4.0811816589,-2.9115937368
C,0,-2.1046940739,-3.5415337029,-3.5021593123
C,0,-1.0901880918,-3.0667652176,-2.670259719
C,0,-1.2239469849,-3.1090384281,-1.2841163166
C,0,-1.9848592183,-3.468822124,-4.999109442
H,0,-2.4784508006,-3.697321984,0.3684319125
H,0,-4.287037887,-4.5736393596,-1.0943861994
H,0,-4.0496468482,-4.4595241538,-3.5485896434
H,0,-0.1869301299,-2.6548421066,-3.1074151066
H,0,-0.4129864941,-2.7318026484,-0.6388400167
H,0,-0.9746827592,-3.1968474879,-5.3042142197
H,0,-2.6736511229,-2.7225674602,-5.4037461898
H,0,-2.2383687867,-4.4265492355,-5.4570846445

N,0,-3.0778011849,-1.0051881626,-1.178212652
O,0,-2.8516241651,-0.6897546217,-0.1353167419
O,0,-3.3848892843,-1.1565743058,-2.2339808555
F,0,2.6157525667,-1.1681255451,-0.600885921
B,0,1.7695188088,-1.0706159708,0.4826736237
F,0,0.8316866103,-2.0863512175,0.4284144674
F,0,2.4914521913,-1.1799034308,1.6512572975
F,0,1.1196901146,0.1455055112,0.4502443406
Pi Complex NO_2BF_4 PCM ONIOM 2.782_93989
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.274781462191

Zero-point correction= 0.158187 (Hartree/Particle)
Thermal correction to Energy= 0.174943
Thermal correction to Enthalpy= 0.175887
Thermal correction to Gibbs Free Energy= 0.110415
Sum of electronic and ZPE= -476.892121
Sum of electronic and thermal Energies= -476.875365
Sum of electronic and thermal Enthalpies= -476.874421
Sum of electronic and thermal Free Energies= -476.939893

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.778 55.625 137.798

C,0,2.4503276908,-1.3334665444,0.9658425561
C,0,3.330018558,-0.9003847672,-0.0274534545
C,0,3.266139398,0.4090513684,-0.483799244
C,0,2.3403381176,1.3201017553,0.048238561
C,0,1.4814653176,0.8832855088,1.0576611443
C,0,1.5272575376,-0.4337247452,1.5110673628
C,0,2.285131852,2.7298578678,-0.4717245886
H,0,2.4965616091,-2.3530960006,1.3315059885
H,0,4.0567893031,-1.5868988017,-0.4452725818
H,0,3.9424873933,0.7398879017,-1.265423794
H,0,0.761760211,1.5736050432,1.4851950337
H,0,0.8537412019,-0.7589521959,2.2967450302
H,0,3.2595596594,3.2138101645,-0.377647259
H,0,1.551819859,3.3262393852,0.0703552723
H,0,2.0181625991,2.7403370126,-1.5313583354
N,0,0.3222945209,-1.5135008382,-0.8185408221
O,0,0.6424896312,-0.6553543387,-1.445254477
O,0,-0.1057004082,-2.4149199452,-0.3241465846
F,0,-2.0432433691,-0.3352939185,-0.6220138399
B,0,-3.0636398249,0.3073150743,0.0616269134
F,0,-3.874016629,0.961773689,-0.8392969159
F,0,-3.7968004428,-0.6274632158,0.7588502173
F,0,-2.5100497856,1.2133815404,0.9395408172

Pi Complex NO_2BF_4 PCM ONIOM 2.788_93809

ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.268745628951

Zero-point correction= 0.157810 (Hartree/Particle)
Thermal correction to Energy= 0.174777
Thermal correction to Enthalpy= 0.175721
Thermal correction to Gibbs Free Energy= 0.109249
Sum of electronic and ZPE= -476.889532
Sum of electronic and thermal Energies= -476.872565
Sum of electronic and thermal Enthalpies= -476.871621
Sum of electronic and thermal Free Energies= -476.938093

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.674 55.744 139.903

C,0,0.9354279697,-0.410030922,1.4317404439
C,0,2.31784071,-0.6127072306,1.4792365674
C,0,3.1697010641,0.2130904951,0.7500657915
C,0,2.6607154837,1.2462294525,-0.0391128238
C,0,1.2727948786,1.4426676169,-0.0719321035
C,0,0.4154224886,0.6305780037,0.6584354003
C,0,3.565973485,2.1318411211,-0.8502289298
H,0,0.2721844789,-1.0424511539,2.0118418376
H,0,2.7276111924,-1.4041367091,2.0966980814
H,0,4.2413384322,0.0523637711,0.7945148922
H,0,0.8659915266,2.2447538818,-0.6794720902
H,0,-0.6595388213,0.7943335746,0.6205470144
H,0,3.3680176706,3.1843553648,-0.6384546215
H,0,3.3969805341,1.9787928851,-1.9191875094
H,0,4.6158285826,1.929826802,-0.6398310147
N,0,1.2774352222,-2.0043377281,-0.8299597963
O,0,0.8702160668,-2.8960344209,-0.3052410517
O,0,1.6848191742,-1.2033389198,-1.4793396838
F,0,-4.5999356621,0.0375245079,-0.3577496832
B,0,-3.2776753874,0.2793765244,-0.0489339485
F,0,-3.1259130519,0.3199385126,1.3214423266
F,0,-2.4988679234,-0.7326941682,-0.5743723401
F,0,-2.8932491142,1.4854527392,-0.5978617587

Pi Complex NO_2BF_4 PCM ONIOM 2.789_94125
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.275819250827

Zero-point correction= 0.157993 (Hartree/Particle)
Thermal correction to Energy= 0.174880
Thermal correction to Enthalpy= 0.175824
Thermal correction to Gibbs Free Energy= 0.110130
Sum of electronic and ZPE= -476.893392
Sum of electronic and thermal Energies= -476.876504

Sum of electronic and thermal Enthalpies= -476.875560
Sum of electronic and thermal Free Energies= -476.941254

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.739 55.802 138.265

C,0,-0.5997583627,-5.0760376813,3.2579206179
C,0,-0.0905813002,-5.8020675744,2.1841753194
C,0,-0.9305564685,-6.6290421181,1.4453519975
C,0,-2.2930087883,-6.7388902043,1.7499477731
C,0,-2.7986772994,-5.9896880467,2.8165781645
C,0,-1.9640388103,-5.1695541705,3.5687013902
C,0,-3.1933439423,-7.6564326882,0.969845457
H,0,0.0463704508,-4.4264348595,3.8372456818
H,0,0.9591393893,-5.7279575041,1.9272296749
H,0,-0.5251775161,-7.2003757629,0.6171480676
H,0,-3.8498439,-6.069291875,3.081368176
H,0,-2.3726880672,-4.6033720609,4.399026112
H,0,-4.1551315111,-7.1817776796,0.769954714
H,0,-3.3920253356,-8.5699937031,1.5369665223
H,0,-2.7433946958,-7.9429639874,0.0197173884
N,0,-0.7854343704,-7.3103841237,4.9168391832
O,0,-0.9540716304,-8.033128443,4.0914479069
O,0,-0.5736135396,-6.7375568559,5.8484440617
F,0,-4.940124909,-7.3887159653,7.1462168667
B,0,-4.6810560777,-7.4514590846,5.7945988752
F,0,-5.3968332425,-6.4738382264,5.139708079
F,0,-3.324140581,-7.2561027165,5.5859012503
F,0,-5.034790392,-8.6920552684,5.3105896203

Pi Complex NO_2BF_4 PCM ONIOM 2.795_93851
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.268316105542

Zero-point correction= 0.157802 (Hartree/Particle)
Thermal correction to Energy= 0.174782
Thermal correction to Enthalpy= 0.175726
Thermal correction to Gibbs Free Energy= 0.108435
Sum of electronic and ZPE= -476.889149
Sum of electronic and thermal Energies= -476.872169
Sum of electronic and thermal Enthalpies= -476.871224
Sum of electronic and thermal Free Energies= -476.938516

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.678 55.717 141.627

C,0,1.347760806,-0.5762478335,1.5557316277
C,0,2.7425629374,-0.5942989719,1.487052328

C,0,3.4064418514,0.3005184172,0.6587833783
C,0,2.7003101839,1.2387581225,-0.1072292925
C,0,1.3071376516,1.2574268087,-0.0190653006
C,0,0.6314423836,0.3574772357,0.8013047783
C,0,3.438373884,2.1916035123,-1.0063327401
H,0,0.8235860863,-1.2653170008,2.2087304888
H,0,3.305643287,-1.3057284057,2.0794609682
H,0,4.4900662466,0.2798199451,0.6032264239
H,0,0.7426696782,1.9818396914,-0.5965909224
H,0,-0.4540764753,0.3900656671,0.8615675164
H,0,2.7694937155,2.9448551827,-1.4218984795
H,0,3.9044816951,1.655536923,-1.8371113743
H,0,4.2351940836,2.701263885,-0.4613565095
N,0,1.1786610847,-1.9395106045,-0.8790110929
O,0,0.3864596141,-2.6141824957,-0.4879993878
O,0,1.9737157124,-1.3592421635,-1.3894902906
F,0,-2.80662585,-0.6395619191,0.7695927324
B,0,-3.4256650692,0.3159077503,-0.0100319235
F,0,-2.4749889724,1.0465617617,-0.6925512263
F,0,-4.2557959631,-0.3069791767,-0.919230792
F,0,-4.1669685712,1.1562336685,0.7935110902

Pi Complex NO_2BF_4 PCM ONIOM 2.805_94148
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.273196595396

Zero-point correction= 0.157623 (Hartree/Particle)
Thermal correction to Energy= 0.174656
Thermal correction to Enthalpy= 0.175600
Thermal correction to Gibbs Free Energy= 0.108064
Sum of electronic and ZPE= -476.891929
Sum of electronic and thermal Energies= -476.874896
Sum of electronic and thermal Enthalpies= -476.873952
Sum of electronic and thermal Free Energies= -476.941488

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	109.598	55.835	142.142

C,0,2.4450375713,-2.3021044858,-0.220467116
C,0,3.224269275,-1.3603091138,-0.8940048413
C,0,4.466557246,-1.0017681909,-0.3878025232
C,0,4.9661254448,-1.5795419436,0.788870782
C,0,4.1864810941,-2.5334036288,1.4445607904
C,0,2.9338527521,-2.8914302653,0.9502211594
C,0,6.3079115558,-1.1609826268,1.3233338292
H,0,1.4762951271,-2.5921743628,-0.6121571215
H,0,2.8598567198,-0.9077086017,-1.8087304075
H,0,5.0665725593,-0.2633892673,-0.9101774215
H,0,4.5570841345,-2.9975660853,2.3523069948

H,0,2.3416583977,-3.637249014,1.4694086814
H,0,7.0767558479,-1.2522769419,0.5535528641
H,0,6.6041235488,-1.767692277,2.1785963556
H,0,6.2878520969,-0.1146547896,1.6389523262
N,0,1.7079839606,-0.4563817864,1.7599557816
O,0,0.6833509713,-0.8799334321,1.8539801683
O,0,2.6787423046,0.0800234823,1.748496263
F,0,1.4890201512,1.8847465083,5.6364305397
B,0,0.689060757,2.2545335404,4.5768400737
F,0,-0.636961972,2.1567534386,4.9376337251
F,0,0.9781176393,3.5498513216,4.2067720124
F,0,0.9317649171,1.4082190218,3.5076030841

Pi Complex NO_2BF_4 PCM ONIOM 2.807_94201
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.268383408515

Zero-point correction= 0.157436 (Hartree/Particle)
Thermal correction to Energy= 0.174783
Thermal correction to Enthalpy= 0.175727
Thermal correction to Gibbs Free Energy= 0.104068
Sum of electronic and ZPE= -476.888647
Sum of electronic and thermal Energies= -476.871301
Sum of electronic and thermal Enthalpies= -476.870357
Sum of electronic and thermal Free Energies= -476.942016

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.678 55.878 150.819

C,0,1.873814788,0.5117575716,-1.7021996179
C,0,2.9561232409,1.2134945715,-1.1610525461
C,0,3.7835373517,0.6064681601,-0.2187959318
C,0,3.543657847,-0.7022145376,0.2042091516
C,0,2.4545638927,-1.3930415524,-0.3448411546
C,0,1.6313275716,-0.8002125816,-1.2941861857
C,0,4.4420531758,-1.3753020171,1.2052965178
H,0,1.2381952537,0.9793060764,-2.4464061252
H,0,3.159689679,2.2283105123,-1.48537368
H,0,4.6234478746,1.1569032465,0.1913046573
H,0,2.2560535838,-2.4099979211,-0.0216549767
H,0,0.7982698074,-1.3541459128,-1.7113606633
H,0,5.0560754068,-0.6513018856,1.7408820684
H,0,5.1125937686,-2.0744119395,0.6987083924
H,0,3.8639333214,-1.9474548916,1.9328608197
N,0,0.7846749666,1.5886001548,0.6512397611
O,0,0.363553945,2.4660497058,0.1142947457
O,0,1.1277937306,0.7609272015,1.3038684196
F,0,-2.7251870558,-0.7365030981,-0.4729179318
B,0,-3.9606345522,-0.5534506728,0.1138996211

F,0,-4.1564035647,-1.5160388928,1.082116977
F,0,-4.0079490864,0.6967276832,0.6963718115
F,0,-4.9442719461,-0.6551569811,-0.8470331303

Pi Complex NO_2BF_4 PCM ONIOM 2.813_93970
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266398676533

Zero-point correction= 0.157694 (Hartree/Particle)
Thermal correction to Energy= 0.174883
Thermal correction to Enthalpy= 0.175828
Thermal correction to Gibbs Free Energy= 0.106798
Sum of electronic and ZPE= -476.888807
Sum of electronic and thermal Energies= -476.871617
Sum of electronic and thermal Enthalpies= -476.870673
Sum of electronic and thermal Free Energies= -476.939703

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.741 55.760 145.286

C,0,-1.3811038169,-4.2686842653,4.6316795158
C,0,-0.0715271929,-4.5105334915,4.2050757943
C,0,0.7370011936,-5.3907133941,4.9124893438
C,0,0.2613162061,-6.0495065892,6.0535232375
C,0,-1.0515766272,-5.8054621194,6.4648398038
C,0,-1.8704447064,-4.9264889573,5.7608446593
C,0,1.1529181978,-6.9998117506,6.804681916
H,0,-2.0194156132,-3.5905392072,4.0759453304
H,0,0.3097891837,-4.0147734153,3.3198373176
H,0,1.7538967059,-5.5731744219,4.5800668683
H,0,-1.4391657594,-6.3030328213,7.3494658783
H,0,-2.8892176797,-4.7547012789,6.0944124127
H,0,0.6657846625,-7.3795337909,7.7024011079
H,0,2.0836437477,-6.5099968645,7.0989940149
H,0,1.4193785124,-7.8521288597,6.1753702084
N,0,-0.2422505678,-2.4729287383,6.4745034811
O,0,0.3970156857,-3.2144421271,6.99264606
O,0,-0.82948522,-1.6392426891,6.033498154
F,0,-2.870880678,-5.7078614558,9.4944408483
B,0,-4.1651132415,-5.2465790242,9.3677683727
F,0,-5.0167306629,-6.3119680973,9.1650054047
F,0,-4.524984347,-4.5788567831,10.5202050536
F,0,-4.2456150826,-4.3805312581,8.2961575167

Pi Complex NO_2BF_4 PCM ONIOM 2.815_94069
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267668627983

Zero-point correction= 0.157398 (Hartree/Particle)

Thermal correction to Energy= 0.174685
Thermal correction to Enthalpy= 0.175629
Thermal correction to Gibbs Free Energy= 0.105358
Sum of electronic and ZPE= -476.888658
Sum of electronic and thermal Energies= -476.871371
Sum of electronic and thermal Enthalpies= -476.870427
Sum of electronic and thermal Free Energies= -476.940698

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.617 55.909 147.898

C,0,4.3896506802,0.1122259262,-3.1759287026
C,0,4.4906212256,1.3444832472,-2.522007904
C,0,4.9880967259,1.4083878875,-1.2224096389
C,0,5.3838045163,0.2503839446,-0.5506908931
C,0,5.2852086509,-0.9769607026,-1.221242538
C,0,4.7997362678,-1.0490068879,-2.521109208
C,0,5.8833757421,0.3060796078,0.866715993
H,0,4.0163588666,0.0632116878,-4.1927630134
H,0,4.1949120624,2.2540824567,-3.0335954836
H,0,5.0676947261,2.3696224836,-0.7258729185
H,0,5.594811672,-1.8843284125,-0.7123360169
H,0,4.7374789786,-2.0072230798,-3.0235163258
H,0,6.1575575769,1.3219892695,1.1511419596
H,0,6.7529344966,-0.3388878933,1.0018995338
H,0,5.1102221743,-0.0393487786,1.5586015152
N,0,1.9857774073,0.2635020379,-1.7171203884
O,0,2.4166545191,-0.1848234216,-0.7999902789
O,0,1.4280073491,0.6972830062,-2.5752332235
F,0,-2.1621417887,-3.0959941737,1.053236947
B,0,-1.2992678299,-2.3429683171,1.8220409637
F,0,-0.053430436,-2.9357038152,1.8260940751
F,0,-1.2003165579,-1.0741318711,1.2883649683
F,0,-1.7762275254,-2.2636247016,3.113345778

Pi Complex NO_2BF_4 PCM ONIOM 2.816_94015
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.268139522516

Zero-point correction= 0.157983 (Hartree/Particle)
Thermal correction to Energy= 0.175170
Thermal correction to Enthalpy= 0.176115
Thermal correction to Gibbs Free Energy= 0.106327
Sum of electronic and ZPE= -476.888503
Sum of electronic and thermal Energies= -476.871315
Sum of electronic and thermal Enthalpies= -476.870371
Sum of electronic and thermal Free Energies= -476.940158

E CV S

KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.921 55.714 146.881

C,0,-1.9113442413,0.7193858841,-1.2652827676
C,0,-2.387462751,0.8551293487,0.0433273605
C,0,-3.2057672665,-0.1271989007,0.5963030201
C,0,-3.5703749947,-1.2536675291,-0.1441671134
C,0,-3.0819798056,-1.3792326774,-1.452059962
C,0,-2.2562946223,-0.4095784881,-2.0080230852
C,0,-4.4823434911,-2.3010727046,0.4328603215
H,0,-1.2589117699,1.4748398347,-1.6885735584
H,0,-2.1067565789,1.7204111074,0.6343599493
H,0,-3.5654756015,-0.0160534951,1.6141082538
H,0,-3.3516448721,-2.253420592,-2.0359019315
H,0,-1.8811163507,-0.5302863101,-3.0174954483
H,0,-4.5047624383,-2.2508993776,1.521472229
H,0,-4.1648461935,-3.3023659721,0.1383401373
H,0,-5.504563602,-2.161478653,0.0698329916
N,0,-4.4417737197,1.9044315182,-1.6225648834
O,0,-4.9860692469,0.9394621893,-1.6518528857
O,0,-4.0183126028,2.9319026125,-1.6445336521
F,0,-7.8610013363,4.1099437352,2.8593632491
B,0,-7.9741436719,2.9242578959,2.1641267002
F,0,-6.9267811376,2.091754511,2.5022211565
F,0,-9.1687830447,2.3127265904,2.4802085977
F,0,-7.9325678607,3.1811224723,0.8087195209

Pi Complex NO_2BF_4 PCM ONIOM 2.817_94021
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.268203592412

Zero-point correction= 0.157942 (Hartree/Particle)
Thermal correction to Energy= 0.175161
Thermal correction to Enthalpy= 0.176105
Thermal correction to Gibbs Free Energy= 0.106148
Sum of electronic and ZPE= -476.888420
Sum of electronic and thermal Energies= -476.871201
Sum of electronic and thermal Enthalpies= -476.870257
Sum of electronic and thermal Free Energies= -476.940213

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.915 55.724 147.237

C,0,3.2760491936,-0.8879710033,-0.9252048117
C,0,2.2043268697,-0.2496363597,-1.5589370835
C,0,1.7511707641,0.9837208904,-1.0965064086
C,0,2.3489571109,1.5969145511,0.0065970155
C,0,3.4250239589,0.948652996,0.6285154259
C,0,3.8908708202,-0.2766252934,0.1672399515

C,0,1.8422554258,2.9108564716,0.5342851741
H,0,3.640677493,-1.8388434413,-1.2972745977
H,0,1.734382432,-0.7091003609,-2.4220091395
H,0,0.9231223906,1.4740137018,-1.5981261439
H,0,3.9034977892,1.4177565709,1.4822166846
H,0,4.7306482066,-0.7565926347,0.6558645007
H,0,1.2008927357,2.7521931326,1.4058887336
H,0,1.2582283221,3.4412695038,-0.2178376725
H,0,2.667502227,3.5516654629,0.8480104685
N,0,1.0499339812,-1.7008949836,0.5977178075
O,0,1.0871192956,-0.8268462671,1.2781476219
O,0,0.9208428743,-2.6371133689,0.0125466021
F,0,-5.0005164593,0.4792774735,-0.2873208908
B,0,-3.7464930501,-0.036602871,-0.038798268
F,0,-2.8241960234,0.9891513917,-0.0021562341
F,0,-3.7456951429,-0.696090603,1.173258157
F,0,-3.4020792148,-0.9231829596,-1.038596893

Pi Complex NO_2BF_4 PCM ONIOM 2.819_94022
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267271057213

Zero-point correction= 0.157573 (Hartree/Particle)
Thermal correction to Energy= 0.174757
Thermal correction to Enthalpy= 0.175702
Thermal correction to Gibbs Free Energy= 0.106144
Sum of electronic and ZPE= -476.888792
Sum of electronic and thermal Energies= -476.871608
Sum of electronic and thermal Enthalpies= -476.870664
Sum of electronic and thermal Free Energies= -476.940221

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.662 55.771 146.396

C,0,-1.7669860373,0.4379928849,1.6813675992
C,0,-3.0153314954,0.0062482909,1.2245687699
C,0,-3.1001829349,-1.0275335024,0.2949122615
C,0,-1.9479003126,-1.6401644101,-0.2015521695
C,0,-0.7023213921,-1.1991180727,0.2672328894
C,0,-0.6088157943,-0.1786269339,1.2045144449
C,0,-2.0234437407,-2.7452911915,-1.2188090827
H,0,-1.7003728637,1.23199539,2.4168393272
H,0,-3.9201419983,0.467702076,1.6043163848
H,0,-4.0731878369,-1.3599304664,-0.0502209435
H,0,0.205788699,-1.661635886,-0.1107780456
H,0,0.3652847634,0.1440708097,1.558072643
H,0,-1.5320065784,-2.4499082547,-2.1490320281
H,0,-3.0560947605,-3.0076994047,-1.447258038
H,0,-1.5145039131,-3.6397941972,-0.8538188721

N,0,-1.9969710108,1.9227085129,-0.7046033113
O,0,-2.2815234095,2.8371142972,-0.1404157681
O,0,-1.7114470382,1.091239348,-1.3786611424
F,0,2.6861565892,-0.7453013892,-0.6569787702
B,0,3.4730834042,0.1745371517,0.0045722384
F,0,4.1018117035,0.9855656127,-0.9180640671
F,0,2.688280302,0.9531850241,0.8305171315
F,0,4.4190016557,-0.4873166893,0.7588895488

Pi Complex NO_2BF_4 PCM ONIOM 2.820_94089
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.275441117371

Zero-point correction= 0.158223 (Hartree/Particle)
Thermal correction to Energy= 0.175036
Thermal correction to Enthalpy= 0.175980
Thermal correction to Gibbs Free Energy= 0.110581
Sum of electronic and ZPE= -476.893256
Sum of electronic and thermal Energies= -476.876444
Sum of electronic and thermal Enthalpies= -476.875499
Sum of electronic and thermal Free Energies= -476.940898

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.837 55.662 137.644

C,0,-1.7803215185,-2.8794586443,-0.9005922701
C,0,-0.5932532638,-2.1544925873,-0.9841913274
C,0,0.4640225373,-2.4553342156,-0.133360647
C,0,0.3696833321,-3.4907065767,0.8070579329
C,0,-0.8177635402,-4.2221032636,0.8720486863
C,0,-1.8868411642,-3.9201280366,0.0306266019
C,0,1.5310657496,-3.8122068412,1.7066259892
H,0,-2.6094680604,-2.6541347282,-1.5614931365
H,0,-0.4969799183,-1.35110102,-1.7044633195
H,0,1.3802879272,-1.8770900598,-0.1926584416
H,0,-0.9234897264,-5.0160419145,1.6063202045
H,0,-2.8041282221,-4.4953191013,0.0990740254
H,0,1.2139336841,-4.3903385982,2.5747448124
H,0,2.0240582743,-2.9035100024,2.0552506985
H,0,2.2753484407,-4.4025662855,1.1660015748
N,0,-2.5781445619,-1.6674288805,1.5185570862
O,0,-1.5404816069,-1.4286397765,1.8307954969
O,0,-3.6690661858,-1.7802372972,1.3253234875
F,0,-2.7362807383,-3.6172676554,3.2601699494
B,0,-3.0061134653,-4.7099738941,4.0703110703
F,0,-2.1123288543,-5.7211666496,3.7960486373
F,0,-2.8894800577,-4.3296578373,5.3894519415
F,0,-4.2900055613,-5.1444231342,3.823409547

Pi Complex NO_2BF_4 PCM ONIOM 2.822_94104
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.275424085266

Zero-point correction= 0.158171 (Hartree/Particle)
Thermal correction to Energy= 0.175004
Thermal correction to Enthalpy= 0.175949
Thermal correction to Gibbs Free Energy= 0.110430
Sum of electronic and ZPE= -476.893308
Sum of electronic and thermal Energies= -476.876474
Sum of electronic and thermal Enthalpies= -476.875530
Sum of electronic and thermal Free Energies= -476.941048

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.817 55.681 137.895

C,0,-2.6552057332,0.7733503251,-1.3523827499
C,0,-1.7921262722,0.4414896821,-0.3004737562
C,0,-1.070800904,1.4362037102,0.3570584502
C,0,-1.1891729967,2.7737897937,-0.0251425435
C,0,-2.0602100957,3.0918555955,-1.0764650335
C,0,-2.792271528,2.1074738352,-1.7302746907
C,0,-0.4198839836,3.8554175132,0.6817531625
H,0,-3.2241100365,-0.0010986385,-1.8540151861
H,0,-1.6828529828,-0.5934291842,0.0060350486
H,0,-0.3871292606,1.1613374935,1.1557015057
H,0,-2.1595714093,4.1272277223,-1.385604238
H,0,-3.4611509871,2.3771609321,-2.5385852632
H,0,-0.0527163013,4.6035935602,-0.022338615
H,0,0.4298388499,3.4468187824,1.2289592785
H,0,-1.0639735202,4.369073867,1.4001194436
N,0,-0.0941434094,0.5028921097,-2.5081823083
O,0,0.1381957321,1.5850196077,-2.4293601441
O,0,-0.1955546064,-0.587389426,-2.7109386673
F,0,1.5258428282,-0.0670363025,-0.5306228491
B,0,2.2671627789,-0.5845943612,0.5208923693
F,0,3.598505616,-0.294796773,0.3160164344
F,0,1.8445552004,-0.0225861251,1.7049812524
F,0,2.0898942215,-1.9501535195,0.5646359999

Pi Complex NO_2BF_4 PCM ONIOM 2.822_94188
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267726128048

Zero-point correction= 0.157544 (Hartree/Particle)
Thermal correction to Energy= 0.174996
Thermal correction to Enthalpy= 0.175940
Thermal correction to Gibbs Free Energy= 0.104331
Sum of electronic and ZPE= -476.888670

Sum of electronic and thermal Energies= -476.871218
Sum of electronic and thermal Enthalpies= -476.870274
Sum of electronic and thermal Free Energies= -476.941883

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.812 55.863 150.715

C,0,3.2546528065,-0.8646636491,1.0061630731
C,0,3.926618121,-0.1942293588,-0.0172370727
C,0,3.4198036664,1.0011001989,-0.5107299886
C,0,2.245254521,1.5619974258,0.0109206889
C,0,1.590913342,0.8920957844,1.0461039597
C,0,2.0858029413,-0.3135651476,1.5402195591
C,0,1.7165545894,2.8565435186,-0.5431426377
H,0,3.6480451498,-1.7945381462,1.4017817563
H,0,4.8401816432,-0.6072665678,-0.4283936546
H,0,3.9397792787,1.5146769924,-1.3132721829
H,0,0.6842580923,1.3127974974,1.4681129899
H,0,1.5690912282,-0.8188899774,2.3491580921
H,0,2.4553150509,3.6528623975,-0.4292037527
H,0,0.8022222222,3.1636450852,-0.0361825585
H,0,1.5023563495,2.7628015444,-1.6103429619
N,0,1.285718981,-1.8085070817,-0.7828164861
O,0,1.2995618386,-0.8971554651,-1.4128621731
O,0,1.1986888377,-2.7824849799,-0.2544809637
F,0,-4.1481838419,0.9584212382,1.0746439388
B,0,-3.8456818419,0.0832959238,0.0525796099
F,0,-4.812781048,-0.8979095633,-0.0156454424
F,0,-3.7972362994,0.7684838918,-1.1437891636
F,0,-2.6194316283,-0.5018935616,0.2942723707

Pi Complex NO_2BF_4 PCM ONIOM 2.823_94179
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267244082575

Zero-point correction= 0.157383 (Hartree/Particle)
Thermal correction to Energy= 0.174822
Thermal correction to Enthalpy= 0.175766
Thermal correction to Gibbs Free Energy= 0.104208
Sum of electronic and ZPE= -476.888618
Sum of electronic and thermal Energies= -476.871179
Sum of electronic and thermal Enthalpies= -476.870235
Sum of electronic and thermal Free Energies= -476.941792

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.702 55.858 150.605

C,0,5.1962954816,-4.9741735147,-0.3333115929

C,0,5.6964274127,-5.0082118601,0.9663022195
C,0,4.9794947648,-5.6535887151,1.9701445209
C,0,3.7616064888,-6.2847424811,1.6976827004
C,0,3.2749848288,-6.2557174392,0.3857246327
C,0,3.9794477751,-5.6051988453,-0.6210607552
C,0,2.9836762095,-6.9818068164,2.7801027777
H,0,5.7535338433,-4.4816073619,-1.1224823926
H,0,6.6416147604,-4.5308582546,1.1972870011
H,0,5.3714606535,-5.6699367689,2.9816481287
H,0,2.3358207151,-6.7482557007,0.1542400177
H,0,3.592701886,-5.5982287897,-1.6344532944
H,0,2.8107101434,-8.0274753402,2.5169120983
H,0,2.0050759491,-6.5155110348,2.9168908484
H,0,3.5116943464,-6.9519649429,3.732939509
N,0,3.3299907571,-2.9653886026,0.3393799282
O,0,3.4320901798,-2.476137967,-0.65290943
O,0,3.1620544064,-3.3498508795,1.3644938649
F,0,-1.203758783,-1.5288416203,2.6860683039
B,0,-0.7345048538,-0.2461215523,2.8810189461
F,0,-1.0002926669,0.1505328977,4.1746525952
F,0,0.6278037004,-0.2191452177,2.6626697212
F,0,-1.3562617984,0.6101134072,1.9963818511

Pi Complex NO_2BF_4 PCM ONIOM 2.825_94068
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267928869545

Zero-point correction= 0.157468 (Hartree/Particle)
Thermal correction to Energy= 0.174778
Thermal correction to Enthalpy= 0.175722
Thermal correction to Gibbs Free Energy= 0.105604
Sum of electronic and ZPE= -476.888824
Sum of electronic and thermal Energies= -476.871515
Sum of electronic and thermal Enthalpies= -476.870570
Sum of electronic and thermal Free Energies= -476.940688

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.675 55.867 147.576

C,0,1.2129154822,-1.1160866734,-0.5547356792
C,0,1.2127612146,-0.9611828235,-1.9411008125
C,0,2.1377672381,-0.1172907274,-2.5437130774
C,0,3.0873667784,0.5795280065,-1.7840138823
C,0,3.0889957467,0.4046072016,-0.3987514585
C,0,2.1594070629,-0.4324406793,0.2149706438
C,0,4.0649531303,1.5059767289,-2.4536176572
H,0,0.5017530644,-1.7818825872,-0.078046863
H,0,0.4923486348,-1.4978610166,-2.5469866574
H,0,2.1303650658,0.0050341866,-3.6220090228

H,0,3.8229293096,0.926450037,0.2064049253
H,0,2.1806116697,-0.5656885873,1.291413887
H,0,3.5734517366,2.439334642,-2.7415063965
H,0,4.4694587227,1.0571782127,-3.362274087
H,0,4.8947298812,1.7547275656,-1.7922114383
N,0,-0.0130906241,1.3964286037,-0.147145753
O,0,0.4762011433,1.8694609155,-1.0220280423
O,0,-0.5864354731,1.0323298985,0.7322539881
F,0,1.561611813,5.4233090971,4.3895379179
B,0,1.1007633187,4.134316172,4.222939407
F,0,0.617052881,3.6561396875,5.4225444849
F,0,0.0894250277,4.1255966473,3.2839806865
F,0,2.1329203755,3.3280201922,3.788785287

Pi Complex NO2BF4 PCM ONIOM 2.826_94040
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267424826797

Zero-point correction= 0.157669 (Hartree/Particle)
Thermal correction to Energy= 0.174927
Thermal correction to Enthalpy= 0.175871
Thermal correction to Gibbs Free Energy= 0.105825
Sum of electronic and ZPE= -476.888564
Sum of electronic and thermal Energies= -476.871307
Sum of electronic and thermal Enthalpies= -476.870362
Sum of electronic and thermal Free Energies= -476.940409

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.768 55.815 147.425

C,0,2.2790254593,-0.8668958293,1.5339750338
C,0,3.3781850835,-0.9515890772,0.6745066042
C,0,3.7157950079,0.1291613466,-0.1375119767
C,0,2.9640216687,1.3050785526,-0.1120336271
C,0,1.8682189355,1.3787955488,0.7595695677
C,0,1.5297192638,0.3102374359,1.5798090349
C,0,3.309030047,2.4747700563,-0.9923642893
H,0,2.0238416631,-1.7023400453,2.1766338681
H,0,3.9778105666,-1.8547864576,0.6500417823
H,0,4.5716492362,0.0557560208,-0.7997908218
H,0,1.2768909519,2.2886395125,0.7905408393
H,0,0.6829510458,0.3883430893,2.2519207369
H,0,2.4608527827,2.7486455889,-1.6239751922
H,0,4.1591052057,2.2518192141,-1.6366793884
H,0,3.5590928304,3.3496821134,-0.3880762362
N,0,1.0603101478,-1.6471592148,-0.8937365881
O,0,1.0309957966,-0.62685003,-1.3247052358
O,0,1.0150440374,-2.7096291945,-0.5708595044
F,0,-3.1858068998,-0.7624580371,-0.6301259266

B,0,-3.9624193907,0.1889397744,-0.0003532794
F,0,-4.9040190038,-0.4370674067,0.7890945535
F,0,-3.1579192064,0.9858342371,0.7878057675
F,0,-4.5937852292,0.9663218018,-0.948431722
Pi Complex NO2BF4 PCM ONIOM 2.829_94116
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266959365789

Zero-point correction= 0.157261 (Hartree/Particle)
Thermal correction to Energy= 0.174598
Thermal correction to Enthalpy= 0.175542
Thermal correction to Gibbs Free Energy= 0.105096
Sum of electronic and ZPE= -476.888998
Sum of electronic and thermal Energies= -476.871661
Sum of electronic and thermal Enthalpies= -476.870717
Sum of electronic and thermal Free Energies= -476.941163

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.562 55.895 148.266

C,0,-5.145308933,-1.5654408088,2.5439999621
C,0,-4.2805325104,-2.6599197471,2.5475041775
C,0,-4.6147720562,-3.8091520978,1.8409282637
C,0,-5.805971514,-3.8877998927,1.1075798322
C,0,-6.6563168283,-2.7795952987,1.0971926514
C,0,-6.3351536829,-1.6280680397,1.8113188849
C,0,-6.1667007474,-5.149727184,0.3731473693
H,0,-4.8858919032,-0.662414665,3.0855366972
H,0,-3.3502796072,-2.6141335772,3.1018224475
H,0,-3.9426773226,-4.6611864806,1.8518499157
H,0,-7.5771402574,-2.8177744502,0.524699499
H,0,-7.0004507501,-0.7719626754,1.7852089065
H,0,-6.6296546558,-5.8692873433,1.0544073413
H,0,-5.2812623642,-5.6246863795,-0.0511617187
H,0,-6.8741594984,-4.9519603634,-0.4322324813
N,0,-6.8986959108,-2.8202246035,4.3762619749
O,0,-6.7530632123,-3.8350038235,3.9557453642
O,0,-7.1130267834,-1.8616726367,4.8955137106
F,0,-7.045775378,-3.9865511185,8.6891262446
B,0,-6.3351899341,-5.0027627844,9.294789567
F,0,-5.708738386,-4.5167989184,10.4229543077
F,0,-7.1982311306,-6.0203034696,9.6436812726
F,0,-5.3882361339,-5.4847593419,8.4144616098

Pi Complex NO2BF4 PCM ONIOM 2.830_93763
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267872230542

Zero-point correction= 0.158479 (Hartree/Particle)

Thermal correction to Energy= 0.175066
Thermal correction to Enthalpy= 0.176010
Thermal correction to Gibbs Free Energy= 0.110018
Sum of electronic and ZPE= -476.889169
Sum of electronic and thermal Energies= -476.872582
Sum of electronic and thermal Enthalpies= -476.871638
Sum of electronic and thermal Free Energies= -476.937630

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.855 55.295 138.892

C,0,-1.0485546681,-2.9668563538,-2.9448666132
C,0,-0.5877366179,-4.1806214114,-2.4424011519
C,0,-0.2190945412,-4.284478622,-1.1037837665
C,0,-0.3152588617,-3.1891842952,-0.2379616737
C,0,-0.7923466484,-1.9778946867,-0.7506376084
C,0,-1.1530227387,-1.8626912037,-2.0889674824
C,0,0.0748239302,-3.2980099046,1.2081705268
H,0,-1.3461803234,-2.8798586104,-3.9837091886
H,0,-0.510924343,-5.0440841207,-3.0924725072
H,0,0.1478181397,-5.2311274791,-0.7215891115
H,0,-0.8804123239,-1.1188452774,-0.0932641402
H,0,-1.5271251644,-0.917905484,-2.4682786715
H,0,-0.7923429506,-3.1278399841,1.8503324649
H,0,0.8344035642,-2.5378173231,1.4802979493
H,0,0.4761818572,-4.2843189531,1.4394048287
N,0,1.5440533851,-1.8325066096,-2.9870770711
O,0,1.313020159,-1.1522081475,-3.8354385837
O,0,1.9069521947,-2.4824127016,-2.1670503173
F,0,3.782330145,-1.8691106323,0.9073327644
B,0,3.3240727208,-1.2632353682,2.0584376823
F,0,3.7837094735,-1.9530867917,3.1596084828
F,0,3.7789575664,0.0380359198,2.101905533
F,0,1.9417630454,-1.2633207596,2.0571953547

Pi Complex NO2BF4 PCM ONIOM 2.830_94055
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266919255288

Zero-point correction= 0.157858 (Hartree/Particle)
Thermal correction to Energy= 0.175081
Thermal correction to Enthalpy= 0.176025
Thermal correction to Gibbs Free Energy= 0.105506
Sum of electronic and ZPE= -476.888207
Sum of electronic and thermal Energies= -476.870984
Sum of electronic and thermal Enthalpies= -476.870040
Sum of electronic and thermal Free Energies= -476.940558

E CV S

KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.865 55.755 148.419

C,0,1.9625589494,-6.6026972739,0.43725645
C,0,2.1016661087,-6.8254354138,1.8107989662
C,0,1.1693010501,-6.3015804574,2.702038984
C,0,0.0888934273,-5.543489451,2.2435344834
C,0,-0.0434695955,-5.3357360536,0.8641937277
C,0,0.8776555142,-5.8620131128,-0.0334784517
C,0,-0.8972968706,-4.936137235,3.2028394124
H,0,2.6790847432,-7.0260032511,-0.2579933052
H,0,2.9291062482,-7.4208016028,2.1808781227
H,0,1.282774766,-6.4840820432,3.7654993205
H,0,-0.8815770363,-4.7535097391,0.4944337203
H,0,0.7530312695,-5.6959509787,-1.0973595131
H,0,-0.8900873992,-5.4539194788,4.1619824209
H,0,-1.9097141123,-4.9684199695,2.7980401178
H,0,-0.6518329636,-3.8863259914,3.3878396112
N,0,3.287948862,-4.2262786185,1.2164681884
O,0,4.2650678278,-4.6068033018,0.8483923867
O,0,2.3748778829,-3.7334020243,1.6042946049
F,0,2.9656704048,1.6683089076,-1.4133419007
B,0,2.5911787464,0.8779945419,-0.3471748567
F,0,2.0379096285,1.6627078172,0.6428468808
F,0,1.6647807988,-0.0535721326,-0.7694761086
F,0,3.6992370496,0.2234774626,0.1518438382

Pi Complex NO2BF4 PCM ONIOM 2.830_94126
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.275092289408

Zero-point correction= 0.158031 (Hartree/Particle)
Thermal correction to Energy= 0.174786
Thermal correction to Enthalpy= 0.175731
Thermal correction to Gibbs Free Energy= 0.110424
Sum of electronic and ZPE= -476.893653
Sum of electronic and thermal Energies= -476.876898
Sum of electronic and thermal Enthalpies= -476.875954
Sum of electronic and thermal Free Energies= -476.941260

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.680 55.684 137.448

C,0,2.5397801517,-0.8425681992,1.0883839021
C,0,3.2780038538,-0.1255860721,0.1523149913
C,0,2.7583829954,1.0445675693,-0.3954398034
C,0,1.5018730632,1.527414271,-0.014832511
C,0,0.7735316391,0.8077229896,0.9378370805
C,0,1.2812498916,-0.3669877538,1.4838977392

C,0,0.9338904142,2.7877946167,-0.6068194001
H,0,2.9380886304,-1.7524372188,1.5223442898
H,0,4.2538162567,-0.479934812,-0.1569052041
H,0,3.3347008753,1.5910568665,-1.1340047562
H,0,-0.2170580731,1.1518832107,1.2277949784
H,0,0.6999780795,-0.9151354795,2.2174978235
H,0,-0.0605696893,2.6072564547,-1.0234026248
H,0,1.5726484277,3.1820804719,-1.3964242772
H,0,0.8274930131,3.5564989205,0.1619633431
N,0,0.6957243948,-1.8234579492,-0.8216760437
O,0,0.4566801065,-2.7465228046,-0.247362658
O,0,0.8683776741,-0.9880480776,-1.5305958235
F,0,-1.6112283502,-0.7953302085,-0.1012904818
B,0,-2.632217863,0.1310427449,0.0553317452
F,0,-2.7359123932,0.4865007019,1.3819908976
F,0,-2.3556909342,1.2431534867,-0.709035804
F,0,-3.814290164,-0.437105729,-0.3671884029

Pi Complex NO2BF4 PCM ONIOM 2.830_94144
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267183559878

Zero-point correction= 0.157622 (Hartree/Particle)
Thermal correction to Energy= 0.174950
Thermal correction to Enthalpy= 0.175894
Thermal correction to Gibbs Free Energy= 0.104563
Sum of electronic and ZPE= -476.888383
Sum of electronic and thermal Energies= -476.871055
Sum of electronic and thermal Enthalpies= -476.870111
Sum of electronic and thermal Free Energies= -476.941441

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.783 55.798 150.128

C,0,2.7772758554,-0.4400459505,-2.7082318387
C,0,1.6545784094,0.3253845703,-3.0270894074
C,0,1.7892193981,1.4520607064,-3.827994494
C,0,3.0383253733,1.8344338587,-4.3380618705
C,0,4.1517025179,1.0529217758,-4.0253513921
C,0,4.0278458525,-0.073704043,-3.2149989157
C,0,3.1602046799,3.0640070707,-5.1954535322
H,0,2.6777596047,-1.3254832459,-2.0901907488
H,0,0.6791696082,0.0423556805,-2.6485177292
H,0,0.9145830054,2.0489389976,-4.0673105596
H,0,5.1254586339,1.3277040057,-4.4166439292
H,0,4.9017515942,-0.6743886465,-2.9872198526
H,0,2.4775844672,3.0107874697,-6.045961549
H,0,4.173989321,3.1854918518,-5.576150218
H,0,2.8995604788,3.959913796,-4.62627019

N,0,3.6889675434,1.4618718201,-0.8203284001
O,0,3.3316399594,2.3380501911,-1.3963212551
O,0,4.0738885085,0.6685562685,-0.1436605165
F,0,0.2541683816,5.0585469393,0.0025122969
B,0,0.528840803,5.2764775793,1.3369173504
F,0,0.2540192135,6.5896024592,1.6553224691
F,0,-0.2483660494,4.4373656819,2.1084004708
F,0,1.86201474,5.0124354632,1.5774429115

Pi Complex NO2BF4 PCM ONIOM 2.831_93989
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266846348776

Zero-point correction= 0.157887 (Hartree/Particle)
Thermal correction to Energy= 0.175085
Thermal correction to Enthalpy= 0.176029
Thermal correction to Gibbs Free Energy= 0.106185
Sum of electronic and ZPE= -476.888195
Sum of electronic and thermal Energies= -476.870997
Sum of electronic and thermal Enthalpies= -476.870053
Sum of electronic and thermal Free Energies= -476.939897

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.867 55.753 147.000

C,0,-3.1405619678,1.0288261601,1.1435492003
C,0,-3.7311585696,0.8124401527,-0.1054177457
C,0,-3.6419409368,-0.4364156949,-0.7140846683
C,0,-2.9597016632,-1.4868625602,-0.0949593145
C,0,-2.380486753,-1.258900934,1.1603305967
C,0,-2.4718194507,-0.0179769461,1.7792632582
C,0,-2.8200630561,-2.8255142055,-0.7659841723
H,0,-3.2256544678,1.9965750365,1.6254152223
H,0,-4.2732137135,1.6149584036,-0.5934965414
H,0,-4.107808408,-0.5961688348,-1.6808284096
H,0,-1.8527181927,-2.0682716163,1.6548046837
H,0,-2.0231276745,0.1355798626,2.7539598052
H,0,-1.8458865969,-2.9058282114,-1.2570083321
H,0,-3.588632825,-2.9724007094,-1.5248263995
H,0,-2.8882112875,-3.6373770232,-0.0406423486
N,0,-0.9205890996,1.4541374785,-0.561506971
O,0,-0.7100395256,0.3767263083,-0.7093548762
O,0,-1.0213046471,2.5577400482,-0.4785386954
F,0,3.4270288679,0.6630400085,-0.7938730352
B,0,4.4189420158,0.0458500932,-0.0592499654
F,0,5.2358420514,-0.6742416349,-0.9052726385
F,0,5.1622930894,1.0028392207,0.5994499208
F,0,3.8438198109,-0.8049424022,0.8619484266

Pi Complex NO2BF4 PCM ONIOM 2.832_93961
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266460911868

Zero-point correction= 0.158104 (Hartree/Particle)
Thermal correction to Energy= 0.175325
Thermal correction to Enthalpy= 0.176269
Thermal correction to Gibbs Free Energy= 0.106450
Sum of electronic and ZPE= -476.887956
Sum of electronic and thermal Energies= -476.870735
Sum of electronic and thermal Enthalpies= -476.869791
Sum of electronic and thermal Free Energies= -476.939610

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 110.018 55.653 146.945

C,0,-2.2315135423,1.0212003264,1.4366720426
C,0,-3.4033421611,1.003918177,0.6769501569
C,0,-3.733326121,-0.1254662852,-0.0644425444
C,0,-2.9103790045,-1.2576175291,-0.058530937
C,0,-1.7433256113,-1.2303820933,0.7123325469
C,0,-1.4044813716,-0.1049727669,1.4566223591
C,0,-3.2907454582,-2.4877444846,-0.8362405713
H,0,-1.975082175,1.8953014401,2.0255057675
H,0,-4.0556431365,1.8695380513,0.6671666131
H,0,-4.6419394082,-0.1320354387,-0.6574301694
H,0,-1.0949958244,-2.100441649,0.7286929698
H,0,-0.5001032363,-0.1031114868,2.0550925187
H,0,-3.8527961062,-2.231886571,-1.735139956
H,0,-3.9236154919,-3.1370295536,-0.2252034963
H,0,-2.4111380822,-3.0632489126,-1.1265903076
N,0,-0.8811012393,1.6363201987,-0.9761390869
O,0,-1.2446694857,0.7571932077,-1.5434523336
O,0,-0.4634450885,2.5547215958,-0.5118057056
F,0,3.7540246217,0.8671086944,-0.719199305
B,0,3.7679308497,-0.2849554515,0.0404648156
F,0,3.4966850426,-1.3674019983,-0.7706190213
F,0,5.0067604598,-0.4407445522,0.6249150976
F,0,2.8030435707,-0.1960909188,1.0228615466

Pi Complex NO2BF4 PCM ONIOM 2.832_94166
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267253721599

Zero-point correction= 0.157324 (Hartree/Particle)
Thermal correction to Energy= 0.174716
Thermal correction to Enthalpy= 0.175660
Thermal correction to Gibbs Free Energy= 0.104439
Sum of electronic and ZPE= -476.888779

Sum of electronic and thermal Energies= -476.871387
Sum of electronic and thermal Enthalpies= -476.870443
Sum of electronic and thermal Free Energies= -476.941664

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.636 55.920 149.897

C,0,-1.4033866266,-0.1769968077,2.8513700684
C,0,-1.610779403,1.1480783862,3.2382760571
C,0,-2.8313514204,1.7600190366,2.9838701182
C,0,-3.8739532484,1.0661154674,2.3534227182
C,0,-3.6603673981,-0.2628922128,1.9830271069
C,0,-2.4357925002,-0.8822483314,2.2257875156
C,0,-5.1890284307,1.7499528056,2.0981974402
H,0,-0.4551609116,-0.6636113509,3.0518849692
H,0,-0.819422532,1.6994103833,3.7327721874
H,0,-2.9869054982,2.7931861456,3.2779949919
H,0,-4.4564058357,-0.818212213,1.498445408
H,0,-2.2870016454,-1.9175784372,1.9387407794
H,0,-5.6824715213,1.9933672869,3.0421164011
H,0,-5.8615665533,1.1188408283,1.5177738154
H,0,-5.0429441733,2.6874399782,1.5573765363
N,0,-1.0902886592,0.5523765275,0.1319378807
O,0,-1.8273085594,1.3786486107,0.1788766242
O,0,-0.3165699409,-0.2272943831,-0.0359112787
F,0,1.9149403985,2.4362466413,-4.884660271
B,0,2.3844108375,2.3543978409,-3.5904959877
F,0,1.7493583272,3.2997533438,-2.8111016291
F,0,2.1224865249,1.0968658962,-3.0864398134
F,0,3.7440210698,2.5835375575,-3.5733615385

Pi Complex NO2BF4 PCM ONIOM 2.833_94062
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267888788648

Zero-point correction= 0.157385 (Hartree/Particle)
Thermal correction to Energy= 0.174709
Thermal correction to Enthalpy= 0.175654
Thermal correction to Gibbs Free Energy= 0.105819
Sum of electronic and ZPE= -476.889058
Sum of electronic and thermal Energies= -476.871734
Sum of electronic and thermal Enthalpies= -476.870789
Sum of electronic and thermal Free Energies= -476.940624

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.632 55.871 146.979

C,0,-5.327080771,-2.3143656504,-1.5331194867
C,0,-6.4669353609,-1.5171785636,-1.4319622358
C,0,-6.4281494778,-0.3432775333,-0.6896832204
C,0,-5.2549781002,0.0681856888,-0.0421377291
C,0,-4.1157455839,-0.7298594661,-0.1608346396
C,0,-4.1483162956,-1.9137534392,-0.8955691496
C,0,-5.2402239513,1.3321163819,0.7727770954
H,0,-5.3462343993,-3.2251164011,-2.1211594079
H,0,-7.3817937226,-1.811743522,-1.9322462167
H,0,-7.3187363139,0.2720820819,-0.61139439
H,0,-3.1955333515,-0.4283618848,0.3318348965
H,0,-3.251578469,-2.5181320079,-0.9846593818
H,0,-5.745061583,2.1429037011,0.2451610074
H,0,-4.2218176908,1.6481658606,0.9984533792
H,0,-5.7641526878,1.184011118,1.7209485816
N,0,-5.5713063036,-3.326076681,1.1020529029
O,0,-6.0922492356,-2.4210497546,1.4736228669
O,0,-5.0955856771,-4.2991898802,0.8531562987
F,0,0.0072686073,-0.5942375954,2.3757495283
B,0,-1.0688258119,-1.1757785244,3.0124840044
F,0,-1.22351094,-2.4731670678,2.5682209344
F,0,-0.8538476634,-1.1783770443,4.3751625563
F,0,-2.213687417,-0.4584876162,2.7323169055

Pi Complex NO2BF4 PCM ONIOM 2.834_93928
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.268482102561

Zero-point correction= 0.158131 (Hartree/Particle)
Thermal correction to Energy= 0.174916
Thermal correction to Enthalpy= 0.175860
Thermal correction to Gibbs Free Energy= 0.109913
Sum of electronic and ZPE= -476.891068
Sum of electronic and thermal Energies= -476.874283
Sum of electronic and thermal Enthalpies= -476.873338
Sum of electronic and thermal Free Energies= -476.939285

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.761 55.484 138.796

C,0,0.7726607136,-2.9688934205,-2.1885951502
C,0,1.6143452466,-2.6817947944,-1.1084418926
C,0,1.0862277674,-2.5082362421,0.1695875128
C,0,-0.2884192991,-2.6105370914,0.3881621798
C,0,-1.1205653723,-2.9053240186,-0.7007064762
C,0,-0.5996413363,-3.0889396543,-1.9756976249
C,0,-0.874346561,-2.3942518823,1.7563537112
H,0,1.1891713792,-3.1197914933,-3.1779142355
H,0,2.685227827,-2.6066030189,-1.2632707745

H,0,1.7570349265,-2.2792238209,1.0155475177
H,0,-2.1900962017,-2.9933534247,-0.5399061782
H,0,-1.259350441,-3.3231923723,-2.8024627344
H,0,-1.4295759293,-1.4533020062,1.7933000912
H,0,-0.0944846797,-2.3562053003,2.5174883091
H,0,-1.5708247864,-3.1940254582,2.0138595053
N,0,0.7399610983,-0.1443022503,-1.9492382049
O,0,-0.1568919619,-0.1412905953,-1.2980689483
O,0,1.6123753395,0.0023427051,-2.6229071541
F,0,2.7671297116,-1.9120373437,2.4223244625
B,0,3.2283815575,-0.6557659741,2.7708228563
F,0,4.6062155572,-0.6467211504,2.7259209776
F,0,2.7345025173,0.2756061295,1.8809095153
F,0,2.802922327,-0.3464883223,4.0446896352

Pi Complex NO2BF4 PCM ONIOM 2.835_94109
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267159007656

Zero-point correction= 0.157421 (Hartree/Particle)
Thermal correction to Energy= 0.174714
Thermal correction to Enthalpy= 0.175658
Thermal correction to Gibbs Free Energy= 0.105166
Sum of electronic and ZPE= -476.888841
Sum of electronic and thermal Energies= -476.871547
Sum of electronic and thermal Enthalpies= -476.870603
Sum of electronic and thermal Free Energies= -476.941096

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.635 55.864 148.364

C,0,-2.6962157279,-2.9646590894,1.5143892758
C,0,-2.4958658871,-4.1776110912,0.8579831096
C,0,-3.5725281401,-5.0276116268,0.626648461
C,0,-4.8673388661,-4.6830455391,1.0323165277
C,0,-5.0592265979,-3.4569621733,1.6757349329
C,0,-3.9863450582,-2.604982258,1.9205375527
C,0,-6.0221909665,-5.619705704,0.8054262567
H,0,-1.8635386352,-2.2920546635,1.6880077417
H,0,-1.5030609911,-4.4593800371,0.5274648085
H,0,-3.4095753126,-5.972576747,0.1188241061
H,0,-6.0573400168,-3.1670878341,1.987985907
H,0,-4.1533406695,-1.6532078066,2.4134239336
H,0,-5.8313846619,-6.2875417562,-0.0348464835
H,0,-6.9433088263,-5.0696708012,0.6099079028
H,0,-6.1911350664,-6.2400813607,1.6902751698
N,0,-2.9229472051,-4.2360195779,4.0387073081
O,0,-3.4094910624,-5.1432117272,3.6295131101
O,0,-2.4212642766,-3.3911080112,4.5568008692

F,0,-5.5273049145,-4.2254290893,7.7893267269
B,0,-6.0238794675,-5.4242292627,8.2592909184
F,0,-5.3524612497,-5.7776413161,9.4108782902
F,0,-7.3697716081,-5.2904258548,8.527675438
F,0,-5.8392989927,-6.4005250725,7.3017801366

Pi Complex NO2BF4 PCM ONIOM 2.838_93889
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.268588814697

Zero-point correction= 0.158392 (Hartree/Particle)
Thermal correction to Energy= 0.174993
Thermal correction to Enthalpy= 0.175937
Thermal correction to Gibbs Free Energy= 0.110740
Sum of electronic and ZPE= -476.891238
Sum of electronic and thermal Energies= -476.874638
Sum of electronic and thermal Enthalpies= -476.873693
Sum of electronic and thermal Free Energies= -476.938890

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.809 55.365 137.217

C,0,-2.8438467912,0.0789393223,1.3104803987
C,0,-3.3039740838,-0.886137535,0.4164014797
C,0,-2.3960849124,-1.6628473563,-0.293468839
C,0,-1.0142578918,-1.5049070251,-0.1190038282
C,0,-0.5621179482,-0.5477904537,0.790275103
C,0,-1.4669375882,0.2416503735,1.4978329933
C,0,-0.0443157526,-2.358398702,-0.8888390653
H,0,-3.5451527896,0.6846127597,1.8725665739
H,0,-4.3680610769,-1.0268283057,0.2694739662
H,0,-2.7594095841,-2.4049056343,-0.9969677337
H,0,0.5227993331,-0.4099205306,0.9387510457
H,0,-1.0998323408,0.9786491304,2.2039513925
H,0,-0.0607578959,-3.3854081772,-0.5162480524
H,0,0.9758169642,-1.9807586485,-0.7925659542
H,0,-0.3037247534,-2.3913072655,-1.9485776823
N,0,-1.989908091,1.8410138478,-0.7444773212
O,0,-1.8727745787,1.0224717684,-1.4823806512
O,0,-2.1065201257,2.7593244302,-0.1280666873
F,0,2.2759089434,-0.2410809212,1.1157272779
B,0,3.0747542002,0.0937325423,0.037059882
F,0,2.3724570581,0.9265635039,-0.8096677411
F,0,4.1981561311,0.7500844993,0.4935506305
F,0,3.4483425742,-1.0469696226,-0.6402331874

Pi Complex NO2BF4 PCM ONIOM 2.839_94082
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267551188633

Zero-point correction= 0.157620 (Hartree/Particle)
Thermal correction to Energy= 0.174939
Thermal correction to Enthalpy= 0.175883
Thermal correction to Gibbs Free Energy= 0.105513
Sum of electronic and ZPE= -476.888717
Sum of electronic and thermal Energies= -476.871398
Sum of electronic and thermal Enthalpies= -476.870454
Sum of electronic and thermal Free Energies= -476.940824

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.776 55.867 148.107

C,0,2.4107074304,-6.946925232,1.7047979307
C,0,1.6206924415,-6.7876849785,2.8438549686
C,0,0.473187116,-6.0071102358,2.7866861979
C,0,0.0795205821,-5.3803491319,1.5957001958
C,0,0.8687884029,-5.5586942249,0.4583461598
C,0,2.0276611083,-6.331547807,0.5092549582
C,0,-1.1648364228,-4.5359902881,1.5628526411
H,0,3.3030346855,-7.5619079642,1.7394378668
H,0,1.9035687265,-7.2696171067,3.7722542582
H,0,-0.1346834129,-5.8802337589,3.6769818035
H,0,0.5774548851,-5.0891889609,-0.4753919034
H,0,2.6261090494,-6.4665391323,-0.3853417117
H,0,-1.3840746413,-4.187372311,0.5540041667
H,0,-1.0572906593,-3.6620697456,2.2102070017
H,0,-2.0248227284,-5.1030973911,1.9248307564
N,0,3.4971879015,-4.334089373,1.9364398202
O,0,4.4822724033,-4.6436846724,1.5254815159
O,0,2.5759344571,-3.9114922598,2.3838366166
F,0,1.5326261433,0.8395975616,-1.6095031904
B,0,2.0748898755,0.1880922712,-0.5220436989
F,0,1.062976047,-0.2498294703,0.3071463485
F,0,2.8119503867,-0.8956556521,-0.9543956897
F,0,2.8966058224,1.0502082637,0.1739776876

Pi Complex NO2BF4 PCM ONIOM 2.839_94167
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266843435738

Zero-point correction= 0.157399 (Hartree/Particle)
Thermal correction to Energy= 0.174840
Thermal correction to Enthalpy= 0.175784
Thermal correction to Gibbs Free Energy= 0.104487
Sum of electronic and ZPE= -476.888762
Sum of electronic and thermal Energies= -476.871321
Sum of electronic and thermal Enthalpies= -476.870377
Sum of electronic and thermal Free Energies= -476.941674

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.714 55.888 150.057

C,0,1.2653940907,-2.9220586745,-0.6295156783
C,0,0.9512768129,-1.6524180218,-1.1144488579
C,0,1.010812828,-1.3978150505,-2.4796567
C,0,1.3689318969,-2.4015904811,-3.3893781246
C,0,1.6706025344,-3.672191629,-2.8935597369
C,0,1.6229272268,-3.9337329002,-1.5263907395
C,0,1.3973234923,-2.1153042783,-4.8658515496
H,0,1.2141461031,-3.1297480625,0.4336844385
H,0,0.6653365727,-0.8640577851,-0.4277525608
H,0,0.7759782664,-0.4054709129,-2.8513865481
H,0,1.9478336113,-4.4635539384,-3.5817497446
H,0,1.8516391626,-4.9275351746,-1.157364715
H,0,0.3860343729,-2.1668215188,-5.2778980581
H,0,2.0123845196,-2.8380155435,-5.4022094176
H,0,1.7810308285,-1.1138653995,-5.0666383559
N,0,4.0470007526,-2.4648708598,-0.9683805041
O,0,4.2894650634,-3.0203387201,-0.0372633228
O,0,3.9283551671,-1.8773735303,-1.89983358
F,0,5.1913632338,1.5821504539,0.0768537288
B,0,4.6887276973,2.7933529427,0.5068539721
F,0,4.8903441498,2.9152684354,1.865800117
F,0,5.3356933167,3.8179359594,-0.1513914984
F,0,3.3375082003,2.8502471893,0.2346978359

Pi Complex NO2BF4 PCM ONIOM 2.841_94092
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267438081587

Zero-point correction= 0.157393 (Hartree/Particle)
Thermal correction to Energy= 0.174751
Thermal correction to Enthalpy= 0.175695
Thermal correction to Gibbs Free Energy= 0.105148
Sum of electronic and ZPE= -476.888677
Sum of electronic and thermal Energies= -476.871319
Sum of electronic and thermal Enthalpies= -476.870375
Sum of electronic and thermal Free Energies= -476.940921

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.658 55.877 148.477

C,0,-0.9498268238,0.1488013235,-2.6976659523
C,0,-0.4347986656,1.3638196916,-2.2452686967
C,0,0.7910391214,1.3959336352,-1.5924953569
C,0,1.5356737822,0.2257304843,-1.386677605

C,0,1.017101652,-0.982170917,-1.8541435662
C,0,-0.2170462525,-1.0253803576,-2.501201098
C,0,2.8612288044,0.2903267608,-0.6785581935
H,0,-1.9019962297,0.1166336893,-3.2157319137
H,0,-0.9911868773,2.2810623818,-2.3993534237
H,0,1.1843396834,2.3423337504,-1.2349743727
H,0,1.5800161495,-1.8985245054,-1.7123736923
H,0,-0.6019084463,-1.971291495,-2.8666290838
H,0,3.5443479848,0.9615632483,-1.2034941831
H,0,3.3289327393,-0.6918784308,-0.6160370411
H,0,2.7415516377,0.6780661989,0.3359103207
N,0,-1.6799412351,-0.7025651746,-0.086548439
O,0,-0.8568598035,-0.1439406071,0.4017420935
O,0,-2.5541579252,-1.2824984015,-0.4525946907
F,0,-4.5670159487,2.2662142778,2.3349294419
B,0,-5.6789108853,1.4518692448,2.4068253936
F,0,-5.3010524171,0.2026537112,2.8546752197
F,0,-6.5968874421,2.0000047247,3.2768944567
F,0,-6.2402780023,1.3360100665,1.1517523826

Pi Complex NO2BF4 PCM ONIOM 2.843_94060
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267764243661

Zero-point correction= 0.157651 (Hartree/Particle)
Thermal correction to Energy= 0.174953
Thermal correction to Enthalpy= 0.175897
Thermal correction to Gibbs Free Energy= 0.105649
Sum of electronic and ZPE= -476.888608
Sum of electronic and thermal Energies= -476.871306
Sum of electronic and thermal Enthalpies= -476.870362
Sum of electronic and thermal Free Energies= -476.940609

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.784 55.816 147.849

C,0,-1.0580609666,-2.4559652005,0.3085246283
C,0,-0.4303701989,-1.2825376753,0.7270509791
C,0,0.5779346572,-1.3384021656,1.6813525642
C,0,0.9922963533,-2.560630001,2.2297343954
C,0,0.3682879644,-3.7298856759,1.7928744528
C,0,-0.6516949894,-3.6820882048,0.8434402157
C,0,2.078022794,-2.5941855166,3.2702317919
H,0,-1.8399145276,-2.4213972123,-0.4418438187
H,0,-0.7295887211,-0.3282040912,0.3098219986
H,0,1.058624698,-0.4222173144,2.0094840706
H,0,0.6776961296,-4.6868687936,2.1996076669
H,0,-1.1220946852,-4.6010120591,0.5099932781
H,0,2.3554240099,-3.6172351435,3.5235848299

H,0,1.7508328866,-2.0939090548,4.1852841214
H,0,2.9702069103,-2.0735418791,2.9168190705
N,0,-2.5603095034,-2.7023144108,2.7105037569
O,0,-1.7999592756,-2.1681778849,3.3139114558
O,0,-3.4054948649,-3.220583252,2.2089152162
F,0,-2.6110073988,-5.1480712438,7.1393338301
B,0,-3.803778217,-4.6119735166,7.5797392968
F,0,-3.7085820103,-4.3178934766,8.92343201
F,0,-4.0742112332,-3.4579420663,6.8730102395
F,0,-4.8189207113,-5.5227104614,7.37373565

Pi Complex NO2BF4 PCM ONIOM 2.844_94005
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267806869155

Zero-point correction= 0.157654 (Hartree/Particle)
Thermal correction to Energy= 0.174839
Thermal correction to Enthalpy= 0.175783
Thermal correction to Gibbs Free Energy= 0.106240
Sum of electronic and ZPE= -476.888644
Sum of electronic and thermal Energies= -476.871459
Sum of electronic and thermal Enthalpies= -476.870515
Sum of electronic and thermal Free Energies= -476.940058

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.713 55.800 146.365

C,0,2.1942053115,-1.3852442795,3.3599499118
C,0,1.8115932607,-0.0582743596,3.5849046843
C,0,0.5394087012,0.2307171721,4.0721858316
C,0,-0.3752235484,-0.7921297685,4.3329146815
C,0,0.0235509272,-2.116716027,4.110462996
C,0,1.295757696,-2.4152311252,3.6354076621
C,0,-1.7668284997,-0.4832530235,4.8129976994
H,0,3.1900547077,-1.6105036185,2.9944781321
H,0,2.5135146687,0.7463811038,3.3948651454
H,0,0.255144906,1.262172556,4.2516393897
H,0,-0.6747754365,-2.9217626007,4.315858454
H,0,1.5864864596,-3.4471344259,3.476114114
H,0,-2.1285171458,-1.2529603917,5.4958337964
H,0,-2.4602698467,-0.4411475139,3.9681374146
H,0,-1.8061968046,0.4793688638,5.3231706539
N,0,0.8362775863,-0.6610406278,0.9673801129
O,0,1.7752285854,-0.3577927026,0.4562300208
O,0,-0.1609431122,-0.9496868675,1.354945962
F,0,2.2008012931,-4.5776507571,-0.3737573414
B,0,1.4238833418,-5.578387186,-0.9208088838
F,0,1.9818455754,-6.8055614456,-0.6315477014
F,0,0.1522485678,-5.5108799747,-0.3895948519

F,0,1.3583365056,-5.4088700004,-2.2881537841

Pi Complex NO2BF4 PCM ONIOM 2.847_94076
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267489098952

Zero-point correction= 0.157625 (Hartree/Particle)
Thermal correction to Energy= 0.174845
Thermal correction to Enthalpy= 0.175789
Thermal correction to Gibbs Free Energy= 0.105907
Sum of electronic and ZPE= -476.889051
Sum of electronic and thermal Energies= -476.871831
Sum of electronic and thermal Enthalpies= -476.870887
Sum of electronic and thermal Free Energies= -476.940769

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.717 55.809 147.080

C,0,1.0886119246,-1.3210842646,-0.6043259189
C,0,1.5228465623,-1.1204796523,-1.9137513397
C,0,2.4386365654,-0.1130514852,-2.1943834395
C,0,2.9505286063,0.7063060137,-1.1796387686
C,0,2.5164210838,0.4910235127,0.1300926137
C,0,1.5921036753,-0.5109338309,0.4189121607
C,0,3.9652379758,1.7701190955,-1.4966594256
H,0,0.3816206094,-2.11097955,-0.376574105
H,0,1.1448872857,-1.7462965169,-2.7134747472
H,0,2.767639525,0.0430724202,-3.2166305994
H,0,2.8996455332,1.115416376,0.9326930944
H,0,1.2710515365,-0.6689402427,1.4432357274
H,0,3.7486366434,2.2516944683,-2.4512899509
H,0,4.9626024319,1.3287359731,-1.5705359059
H,0,3.9970639645,2.5347048212,-0.7201977274
N,0,-0.593976574,0.9756869195,-0.6229601076
O,0,0.0247505345,1.4980712341,-1.3792993468
O,0,-1.3138836308,0.5457434294,0.1060929877
F,0,2.7048268145,5.0391601545,3.2193681762
B,0,2.0356664012,3.8375504491,3.1202117205
F,0,2.9339403668,2.8319017557,2.8294346303
F,0,1.4047485443,3.5576695269,4.3145324226
F,0,1.0937516201,3.9170163927,2.1144718489

Pi Complex NO2BF4 PCM ONIOM 2.852_94057
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267430511131

Zero-point correction= 0.157373 (Hartree/Particle)
Thermal correction to Energy= 0.174705
Thermal correction to Enthalpy= 0.175649

Thermal correction to Gibbs Free Energy= 0.106061
Sum of electronic and ZPE= -476.889258
Sum of electronic and thermal Energies= -476.871925
Sum of electronic and thermal Enthalpies= -476.870981
Sum of electronic and thermal Free Energies= -476.940570

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.629 55.872 146.461

C,0,1.1765873625,-1.4681046311,4.3651804359
C,0,1.1374317459,-0.1859148568,4.9215125012
C,0,-0.081018914,0.4699777534,5.086426603
C,0,-1.2761546142,-0.134936249,4.6938391043
C,0,-1.222518143,-1.4216132357,4.1405851112
C,0,-0.0129125006,-2.0871430858,3.9816301277
C,0,-2.5950048962,0.5738352287,4.8393244495
H,0,2.1232101452,-1.9853876458,4.2535360872
H,0,2.056835919,0.2922389209,5.2418607007
H,0,-0.1011479105,1.4609860205,5.5270110771
H,0,-2.1454738337,-1.9047105288,3.835549046
H,0,0.0071136108,-3.0850276491,3.5553011158
H,0,-2.5131241834,1.4358807462,5.5012172028
H,0,-3.3559822223,-0.0979245318,5.2399613234
H,0,-2.9514176677,0.9267286223,3.8677075715
N,0,1.180610284,0.2799944363,2.1110506019
O,0,2.2897414499,0.3275438258,2.0687689064
O,0,0.0752870687,0.2956232251,2.0366619484
F,0,0.8394202973,-4.9590183903,2.0033441071
B,0,1.0171073966,-4.8851970992,0.6374053669
F,0,-0.0105279649,-5.5499914432,0.0019065238
F,0,1.0189925588,-3.5617811043,0.2453458468
F,0,2.2228641115,-5.4627118282,0.2983561412

Pi Complex NO2BF4 PCM ONIOM 2.852_94125
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267003972576

Zero-point correction= 0.157376 (Hartree/Particle)
Thermal correction to Energy= 0.174698
Thermal correction to Enthalpy= 0.175642
Thermal correction to Gibbs Free Energy= 0.104863
Sum of electronic and ZPE= -476.888746
Sum of electronic and thermal Energies= -476.871424
Sum of electronic and thermal Enthalpies= -476.870479
Sum of electronic and thermal Free Energies= -476.941259

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.625 55.860 148.967

C,0,1.0533877984,1.052220148,-3.8255433203
C,0,1.1336209068,2.3737914375,-3.3763584345
C,0,2.1925087513,2.774323573,-2.5641278113
C,0,3.1813481689,1.8665533184,-2.1801598071
C,0,3.0923132082,0.5468670178,-2.6435437559
C,0,2.0448185398,0.1409939918,-3.4615518299
C,0,4.3083074235,2.2787068699,-1.2732054026
H,0,0.23818017,0.7449561186,-4.4712640992
H,0,0.3776935003,3.0929680415,-3.6727436109
H,0,2.2498942787,3.8035791913,-2.2255814088
H,0,3.8581000494,-0.1668894587,-2.3568987869
H,0,1.9974374028,-0.8826792089,-3.8140930403
H,0,4.1489208679,1.8904899369,-0.2633878603
H,0,4.3880836079,3.363680643,-1.2062173407
H,0,5.2611004176,1.8827755775,-1.6280873177
N,0,-0.1611616932,0.9235559751,-1.2477323384
O,0,-1.1835478692,1.0496205904,-1.6635949681
O,0,0.8030178718,0.7648082589,-0.7258186356
F,0,-1.4335826944,3.2350879375,3.3625804084
B,0,-2.3993649085,2.255590851,3.4711000644
F,0,-1.9557698524,1.1062746063,2.8490257742
F,0,-2.6444756826,1.9915503442,4.8019045599
F,0,-3.5589014629,2.687223739,2.8608416613

Pi Complex NO2BF4 PCM ONIOM 2.854_93769
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267971080380

Zero-point correction= 0.157854 (Hartree/Particle)
Thermal correction to Energy= 0.174755
Thermal correction to Enthalpy= 0.175699
Thermal correction to Gibbs Free Energy= 0.109794
Sum of electronic and ZPE= -476.889639
Sum of electronic and thermal Energies= -476.872738
Sum of electronic and thermal Enthalpies= -476.871794
Sum of electronic and thermal Free Energies= -476.937699

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.660 55.737 138.708

C,0,2.7553538367,-0.198961917,1.3372238879
C,0,3.3258572958,0.7801018919,0.5248642283
C,0,2.5105376518,1.6474685433,-0.1919251339
C,0,1.1133521027,1.5673515608,-0.1086845312
C,0,0.5522843723,0.5917904341,0.7162680778
C,0,1.363034637,-0.2872211992,1.4330457024
C,0,0.2494893426,2.5220048501,-0.885842256
H,0,3.3841319584,-0.8725288395,1.9083455919

H,0,4.4036195937,0.8631021455,0.4497772378
H,0,2.9587779522,2.4026502504,-0.8295100685
H,0,-0.5312234496,0.5093867131,0.7902335866
H,0,0.910947589,-1.0337699343,2.0772613487
H,0,0.543556564,2.5500119553,-1.9370726564
H,0,0.3517105845,3.5356377429,-0.4911761859
H,0,-0.8033954777,2.2413741111,-0.8283947835
N,0,1.9273248289,-1.8230235427,-0.8596625642
O,0,1.9542851221,-2.771607445,-0.2811737728
O,0,1.8993772614,-0.958886932,-1.5526305762
F,0,-4.3974545784,-0.5212622008,-0.2611253365
B,0,-3.1033333808,-0.1677035455,0.0612832334
F,0,-2.758674659,-0.7534819971,1.2626910324
F,0,-2.254039682,-0.6183969181,-0.9294044052
F,0,-3.0157134655,1.2043972731,0.1671073431

Pi Complex NO2BF4 PCM ONIOM 2.857_93993
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266420595424

Zero-point correction= 0.157772 (Hartree/Particle)
Thermal correction to Energy= 0.175035
Thermal correction to Enthalpy= 0.175979
Thermal correction to Gibbs Free Energy= 0.105984
Sum of electronic and ZPE= -476.888151
Sum of electronic and thermal Energies= -476.870887
Sum of electronic and thermal Enthalpies= -476.869943
Sum of electronic and thermal Free Energies= -476.939939

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.836 55.752 147.318

C,0,4.3078648248,1.2113217647,-2.9354043091
C,0,3.8376258835,2.0373701879,-1.9108266205
C,0,4.1477208932,1.7508318466,-0.5827940204
C,0,4.9238091917,0.6377031189,-0.2538899533
C,0,5.3953900837,-0.1778202419,-1.2922114132
C,0,5.0982383638,0.1047359123,-2.619304369
C,0,5.2437350394,0.2999913598,1.176478912
H,0,4.0790616431,1.4423398634,-3.9697698938
H,0,3.239518964,2.9100550864,-2.1497125617
H,0,3.7791714022,2.3986315874,0.2057173441
H,0,6.0042761798,-1.0431867161,-1.0500161532
H,0,5.4785503625,-0.5336952638,-3.408248061
H,0,4.9133229966,1.0856523036,1.855499186
H,0,6.3178196619,0.1581238326,1.3109189387
H,0,4.7536263307,-0.6317449569,1.4708479177
N,0,1.9347741374,-0.1488274358,-2.1093999303
O,0,2.4353133454,-0.6665175799,-1.2680408039

O,0,1.3397366423,0.2980943648,-2.9341771269
F,0,-2.6375085414,-3.0409677594,1.616614049
B,0,-1.4030592938,-2.4648761402,1.8318565276
F,0,-0.471532643,-3.4498238347,2.0871838324
F,0,-1.0265013838,-1.7586501341,0.7074253349
F,0,-1.473480684,-1.6067336659,2.9094934739

Pi Complex NO2BF4 PCM ONIOM 2.858_94149
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267212235626

Zero-point correction= 0.157311 (Hartree/Particle)
Thermal correction to Energy= 0.174683
Thermal correction to Enthalpy= 0.175627
Thermal correction to Gibbs Free Energy= 0.104611
Sum of electronic and ZPE= -476.888790
Sum of electronic and thermal Energies= -476.871418
Sum of electronic and thermal Enthalpies= -476.870474
Sum of electronic and thermal Free Energies= -476.941490

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.615 55.862 149.466

C,0,-4.8384392429,-1.4150876179,0.1284602354
C,0,-4.3742645313,-0.7529209657,1.2686537305
C,0,-4.154922022,0.6237405457,1.2401854542
C,0,-4.3866327247,1.3599692679,0.0778581546
C,0,-4.8560897798,0.6836460963,-1.0570155443
C,0,-5.0860238066,-0.6864568093,-1.034939501
C,0,-4.1402246379,2.8431184245,0.0273716266
H,0,-5.0242988681,-2.4828236825,0.1559669735
H,0,-4.1953515855,-1.3080056309,2.1834173868
H,0,-3.7978301458,1.1276917,2.1320724356
H,0,-5.0455124796,1.2446645769,-1.9667789826
H,0,-5.4559477593,-1.1877974223,-1.9215840552
H,0,-3.8175738502,3.2266734996,0.9949986786
H,0,-5.0470048615,3.375534316,-0.267076848
H,0,-3.3694579689,3.0829410946,-0.7091961955
N,0,-2.001233,-1.3090130104,-0.2025591199
O,0,-2.0465042616,-0.3556777563,-0.7649870836
O,0,-1.8345194515,-2.2756148764,0.3189675604
F,0,3.5258950395,1.0410899965,-1.0660239005
B,0,3.2460632915,0.249376204,0.0282409688
F,0,4.4104378164,-0.3162226392,0.503221206
F,0,2.6691827088,1.0196062087,1.0171572256
F,0,2.368976121,-0.7502735199,-0.3410174059

Pi Complex NO2BF4 PCM ONIOM 2.866_94198
ONIOM(M062X/6-311G*:PM3)

E(RPM3) = 0.266440956603

Zero-point correction= 0.157232 (Hartree/Particle)
Thermal correction to Energy= 0.174589
Thermal correction to Enthalpy= 0.175533
Thermal correction to Gibbs Free Energy= 0.104205
Sum of electronic and ZPE= -476.888952
Sum of electronic and thermal Energies= -476.871596
Sum of electronic and thermal Enthalpies= -476.870652
Sum of electronic and thermal Free Energies= -476.941980

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.556 55.911 150.123

C,0,-3.8136900644,0.307942171,0.8369737673
C,0,-3.8952767669,0.2986889649,-0.5589152874
C,0,-3.5093664397,-0.8315794418,-1.2754862269
C,0,-3.0287083219,-1.9659158287,-0.6171628422
C,0,-2.9598605705,-1.9458072019,0.7818427778
C,0,-3.352030945,-0.8253729587,1.5055422655
C,0,-2.5664575853,-3.1728024254,-1.3867261936
H,0,-4.1310678404,1.1818240095,1.3949994825
H,0,-4.2766350615,1.1673114754,-1.0848269785
H,0,-3.5830837718,-0.8318035791,-2.357974237
H,0,-2.5935325812,-2.8220739201,1.3072277131
H,0,-3.2976361227,-0.8331770204,2.5878880654
H,0,-1.4801694695,-3.1513266023,-1.5131119151
H,0,-3.0152457646,-3.206755874,-2.3795203398
H,0,-2.8166825375,-4.0948035021,-0.8604132453
N,0,-1.163284515,1.0380206594,0.0256362307
O,0,-0.8315487524,-0.0146846932,-0.065861352
O,0,-1.3845857401,2.12346682,0.104886118
F,0,3.2052012388,1.8058337968,1.5254638272
B,0,4.1396869612,1.8320325077,0.5104236338
F,0,4.3283475484,3.1339107203,0.0957371993
F,0,5.3320398342,1.3120960376,0.9675911875
F,0,3.683539268,1.0756908851,-0.5497956503

Pi Complex NO2BF4 PCM ONIOM 2.868_93751
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267565186050

Zero-point correction= 0.157873 (Hartree/Particle)
Thermal correction to Energy= 0.174743
Thermal correction to Enthalpy= 0.175687
Thermal correction to Gibbs Free Energy= 0.110136
Sum of electronic and ZPE= -476.889778
Sum of electronic and thermal Energies= -476.872908

Sum of electronic and thermal Enthalpies= -476.871964
Sum of electronic and thermal Free Energies= -476.937515

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.653 55.678 137.965

C,0,-2.6907653831,0.3514104063,1.3517733719
C,0,-3.3717120662,-0.5687835594,0.5569313789
C,0,-2.660318391,-1.5036510775,-0.1865985961
C,0,-1.2606773915,-1.5500480594,-0.1470711834
C,0,-0.5883562619,-0.6308696258,0.6608059143
C,0,-1.2934593279,0.3139711857,1.4036396422
C,0,-0.5063486408,-2.5819949226,-0.9398946995
H,0,-3.2385653023,1.0785355805,1.9403404829
H,0,-4.45419975,-0.5539048432,0.5150878121
H,0,-3.1955397274,-2.2123207442,-0.8100853138
H,0,0.5000418679,-0.6432407211,0.6996164899
H,0,-0.7555448624,1.0168888362,2.0307445533
H,0,-0.9681446161,-2.7479502805,-1.9142263427
H,0,-0.5039878669,-3.5379148988,-0.4097741722
H,0,0.532193011,-2.2841833879,-1.0933318466
N,0,-1.7971772942,1.8959298908,-0.8945078626
O,0,-1.8289155221,1.0259609964,-1.5795917288
O,0,-1.7616881584,2.8455306381,-0.3186119953
F,0,4.4184015092,0.3763205706,-0.0835801347
B,0,3.1060910193,0.0304408181,0.1637522467
F,0,3.0471474345,-0.7910762469,1.2702723725
F,0,2.3710885413,1.1763638974,0.3932505017
F,0,2.5967601792,-0.6327504528,-0.9341348906

Pi Complex NO2BF4 PCM ONIOM 2.870_93870
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267106987355

Zero-point correction= 0.157891 (Hartree/Particle)
Thermal correction to Energy= 0.174886
Thermal correction to Enthalpy= 0.175830
Thermal correction to Gibbs Free Energy= 0.108833
Sum of electronic and ZPE= -476.889649
Sum of electronic and thermal Energies= -476.872655
Sum of electronic and thermal Enthalpies= -476.871711
Sum of electronic and thermal Free Energies= -476.938708

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.742 55.711 141.007

C,0,-3.0726268251,0.2434256471,1.1789611709
C,0,-1.7652802339,-0.1226934507,1.5151368245

C,0,-0.6829099106,0.4773827226,0.8743512526
C,0,-0.8830397662,1.4449163057,-0.112429186
C,0,-2.1977582307,1.8047042247,-0.436763265
C,0,-3.2828851151,1.2176148917,0.2042456635
C,0,0.2836504966,2.1014591146,-0.7974804032
H,0,-3.9136842849,-0.2119900771,1.6890065323
H,0,-1.5924473426,-0.8680828057,2.2841180223
H,0,0.3321396696,0.184649922,1.1337971517
H,0,-2.3674915585,2.5556818484,-1.201534236
H,0,-4.2916171254,1.5139110965,-0.0578442707
H,0,0.4641773879,3.0914648457,-0.3708371695
H,0,0.0940832686,2.2343705525,-1.8637050883
H,0,1.1971800696,1.5130541866,-0.6754910647
N,0,-2.3185280309,-1.7721844905,-0.720501478
O,0,-1.9992722711,-1.0181999883,-1.466256975
O,0,-2.6382088694,-2.6156131476,-0.0718637816
F,0,2.1580477125,-1.0553816274,-0.3537952855
B,0,3.2403365736,-0.2908113164,0.0322473669
F,0,4.2900198185,-1.1291338791,0.349888683
F,0,3.6178509213,0.5365612161,-1.0053430703
F,0,2.9146996462,0.4656452084,1.1387856061

Pi Complex NO2BF4 PCM ONIOM 2.875_94070
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267228760185

Zero-point correction= 0.157816 (Hartree/Particle)
Thermal correction to Energy= 0.175116
Thermal correction to Enthalpy= 0.176060
Thermal correction to Gibbs Free Energy= 0.105422
Sum of electronic and ZPE= -476.888312
Sum of electronic and thermal Energies= -476.871012
Sum of electronic and thermal Enthalpies= -476.870068
Sum of electronic and thermal Free Energies= -476.940706

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.887 55.757 148.671

C,0,3.9063366737,1.8716672295,-2.5472638222
C,0,3.2595686218,2.4558972071,-1.454105135
C,0,3.5565886726,2.0388736206,-0.1570262823
C,0,4.4930763259,1.0299489463,0.0716463762
C,0,5.1374977209,0.4559524866,-1.0335922867
C,0,4.855414587,0.8731890255,-2.3286656114
C,0,4.8043772835,0.550541988,1.4630658512
H,0,3.6869548577,2.2080075743,-3.5543958528
H,0,2.5349644099,3.2475311134,-1.6125003726
H,0,3.0525299813,2.5034799522,0.6840262131
H,0,5.8713605531,-0.3268288617,-0.8695688829

H,0,5.3701530814,0.4205861333,-3.168149197
H,0,4.327408746,1.1774050948,2.21625984
H,0,5.8810277656,0.5541583047,1.6433378055
H,0,4.4543982113,-0.4753260398,1.6043439426
N,0,1.6865084997,0.1400862977,-1.9620599263
O,0,2.3171295349,-0.5089891322,-1.3234808367
O,0,0.9705207846,0.6976293123,-2.6029607252
F,0,-2.4443684265,-2.745850379,1.0760550798
B,0,-1.1388073593,-3.1222488309,1.3139497992
F,0,-1.1178539449,-4.3015006529,2.0280480536
F,0,-0.4878963034,-3.2997910789,0.1101943028
F,0,-0.5021773771,-2.1338570109,2.0362481671

Pi Complex NO2BF4 PCM ONIOM 2.877_93769
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267132492595

Zero-point correction= 0.158214 (Hartree/Particle)
Thermal correction to Energy= 0.175249
Thermal correction to Enthalpy= 0.176193
Thermal correction to Gibbs Free Energy= 0.108904
Sum of electronic and ZPE= -476.888387
Sum of electronic and thermal Energies= -476.871352
Sum of electronic and thermal Enthalpies= -476.870408
Sum of electronic and thermal Free Energies= -476.937697

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.970 55.674 141.622

C,0,3.5600583301,0.2360311215,-0.5485453573
C,0,3.5691628392,-0.5120834574,0.6265622054
C,0,2.5457381593,-1.4202205065,0.8806666167
C,0,1.5019893464,-1.6114760155,-0.0330785499
C,0,1.512955265,-0.8700160923,-1.2174212196
C,0,2.5268121046,0.050208258,-1.473634309
C,0,0.3785717348,-2.5659023481,0.2651553492
H,0,4.3579826109,0.939592477,-0.7571901731
H,0,4.3707498585,-0.3856817745,1.3447122547
H,0,2.5555196279,-1.994145376,1.8016029397
H,0,0.7204284479,-1.0123526832,-1.9451426719
H,0,2.5229300503,0.6128416584,-2.4011259489
H,0,-0.4476460795,-2.0417103124,0.7564401765
H,0,0.7029403337,-3.3672877719,0.929195427
H,0,-0.0141372173,-3.0105266486,-0.6499249687
N,0,1.4204206188,1.9424624293,0.3409278053
O,0,1.063837783,1.1759898313,1.0564163441
O,0,1.7115086485,2.7944247688,-0.309740515
F,0,-2.6783610682,-0.6230737556,0.7853921775
B,0,-3.4901165659,0.1666474056,-0.0020962089

F,0,-2.7109938701,0.8921505164,-0.8805397199
F,0,-4.3634839345,-0.630384603,-0.7114961475
F,0,-4.2022260233,1.0345468786,0.7996964936

Pi Complex NO2BF4 PCM ONIOM 2.879_94110
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267312400944

Zero-point correction= 0.157856 (Hartree/Particle)
Thermal correction to Energy= 0.175140
Thermal correction to Enthalpy= 0.176084
Thermal correction to Gibbs Free Energy= 0.105343
Sum of electronic and ZPE= -476.888595
Sum of electronic and thermal Energies= -476.871311
Sum of electronic and thermal Enthalpies= -476.870367
Sum of electronic and thermal Free Energies= -476.941108

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.902 55.791 148.886

C,0,2.3083781926,-1.5427545649,-3.1785996808
C,0,1.183877978,-2.1108516881,-2.5718267043
C,0,-0.0910376385,-1.6293078715,-2.8656764107
C,0,-0.2664834394,-0.5705761356,-3.7586560596
C,0,0.8689657953,-0.0137720755,-4.3626819607
C,0,2.1430965061,-0.4949249032,-4.0831644294
C,0,-1.6344322979,-0.0182190646,-4.0526132991
H,0,3.2976788305,-1.9308567809,-2.963837944
H,0,1.3013569861,-2.9402412115,-1.8823252601
H,0,-0.9573597347,-2.081967345,-2.3942503078
H,0,0.7473240876,0.8059878752,-5.0635735845
H,0,3.0066997948,-0.0553292023,-4.5682082009
H,0,-2.4168235771,-0.7111022917,-3.743281879
H,0,-1.7548587366,0.1868895865,-5.1173714432
H,0,-1.7896523917,0.9234639211,-3.5187452915
N,0,1.7465624658,0.1019913275,-0.8833036314
O,0,1.1718960956,0.8224032438,-1.4977983368
O,0,2.3287653218,-0.530132726,-0.1795018677
F,0,-1.8525684677,0.998772266,1.6233323397
B,0,-3.0596377601,0.346963077,1.4722792451
F,0,-3.2794976153,-0.4678694556,2.5630659531
F,0,-4.0740054717,1.2759734021,1.3754209878
F,0,-3.0229326237,-0.4199984828,0.3259213659

Pi Complex NO2BF4 PCM ONIOM 2.889_93857
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267215216048

Zero-point correction= 0.157833 (Hartree/Particle)

Thermal correction to Energy= 0.174796
Thermal correction to Enthalpy= 0.175741
Thermal correction to Gibbs Free Energy= 0.108931
Sum of electronic and ZPE= -476.889667
Sum of electronic and thermal Energies= -476.872704
Sum of electronic and thermal Enthalpies= -476.871760
Sum of electronic and thermal Free Energies= -476.938570

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.686 55.699 140.613

C,0,-3.2903349793,-0.0131094848,-0.9143924832
C,0,-2.0445521491,0.1751166832,-1.5247712822
C,0,-0.9390410774,-0.555506486,-1.0992051722
C,0,-1.049288102,-1.4797622204,-0.0557585117
C,0,-2.3012461536,-1.6608100117,0.5423600667
C,0,-3.4143214415,-0.9410538808,0.1158122432
C,0,0.1522729598,-2.2646195103,0.393978568
H,0,-4.1535924382,0.5475133085,-1.2545147832
H,0,-1.9422512217,0.8854968422,-2.3382198156
H,0,0.0260685536,-0.4020207066,-1.5745839405
H,0,-2.4026209791,-2.3734218404,1.354170663
H,0,-4.3754477637,-1.1000664774,0.5900934396
H,0,1.0453851305,-1.6324062597,0.4332995873
H,0,0.3591433605,-3.0762566082,-0.3082826055
H,0,-0.0043090609,-2.706499656,1.3778786659
N,0,-1.8719165659,1.887932334,0.7350351096
O,0,-2.1766785815,2.7665601626,0.127486182
O,0,-1.5403605156,1.0933069489,1.431171867
F,0,2.43397362,0.5524007251,1.1380924878
B,0,3.2284269513,0.0839757902,0.1109978883
F,0,2.5071835654,0.0783765561,-1.0654887149
F,0,4.3189493689,0.9177487086,-0.0317655468
F,0,3.6630895194,-1.191828917,0.4024840875

Pi Complex NO2BF4 PCM ONIOM 2.894_93761
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266705108122

Zero-point correction= 0.157922 (Hartree/Particle)
Thermal correction to Energy= 0.174787
Thermal correction to Enthalpy= 0.175731
Thermal correction to Gibbs Free Energy= 0.109908
Sum of electronic and ZPE= -476.889605
Sum of electronic and thermal Energies= -476.872740
Sum of electronic and thermal Enthalpies= -476.871796
Sum of electronic and thermal Free Energies= -476.937619

E CV S

KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.680 55.655 138.536

C,0,-3.290833929,-0.1041857649,-0.863687202
C,0,-2.0520809325,0.1156419655,-1.4756273807
C,0,-0.9223027046,-0.5696198712,-1.035604206
C,0,-1.0024169476,-1.4760103325,0.0246595678
C,0,-2.2493102616,-1.6890300125,0.6252724544
C,0,-3.3851967966,-1.0178728816,0.1836456544
C,0,0.2187227312,-2.2179006052,0.4943197688
H,0,-4.172659547,0.4187798819,-1.2156936594
H,0,-1.9724021059,0.8143487399,-2.3017106793
H,0,0.0370536913,-0.3948454519,-1.5153436692
H,0,-2.326622883,-2.3898776746,1.450052148
H,0,-4.3411338259,-1.200131896,0.6603162131
H,0,0.1549819724,-2.455536982,1.5567551992
H,0,1.1284573267,-1.6349930875,0.32132807
H,0,0.3219065777,-3.1607622083,-0.0491414693
N,0,-1.9548516622,1.8756369103,0.7710677127
O,0,-1.5819662465,1.1006136618,1.4683284053
O,0,-2.3045345313,2.7340579959,0.1590453969
F,0,2.3785317257,0.7594766002,0.7204649682
B,0,3.2482333738,0.1321744487,-0.1488554229
F,0,4.3055661284,0.978446212,-0.4149572839
F,0,3.7239720269,-1.026710411,0.4281832985
F,0,2.5966488194,-0.1617422372,-1.3289188846

Pi Complex NO2BF4 PCM ONIOM 3.045_94107
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.265798563610

Zero-point correction= 0.157612 (Hartree/Particle)
Thermal correction to Energy= 0.175016
Thermal correction to Enthalpy= 0.175960
Thermal correction to Gibbs Free Energy= 0.104633
Sum of electronic and ZPE= -476.888095
Sum of electronic and thermal Energies= -476.870691
Sum of electronic and thermal Enthalpies= -476.869747
Sum of electronic and thermal Free Energies= -476.941074

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.824 55.769 150.121

C,0,-3.8124303407,1.2448895021,0.5638065754
C,0,-3.6057436488,0.9523810035,-0.7849633239
C,0,-3.2252538928,-0.3331504761,-1.1782828127
C,0,-3.0434906309,-1.3446240607,-0.234431079
C,0,-3.2518128455,-1.0359617659,1.1158485992
C,0,-3.6349833918,0.2408547961,1.5138539533

C,0,-2.6438621259,-2.7365841106,-0.6438832669
H,0,-4.1201254284,2.2389135962,0.8663802518
H,0,-3.7538663513,1.721147417,-1.5361124031
H,0,-3.0760641097,-0.5485902259,-2.2313468515
H,0,-3.1119677011,-1.8109173441,1.8631531543
H,0,-3.7943231966,0.4532091269,2.5645894294
H,0,-3.4519139521,-3.4426259949,-0.4391682278
H,0,-1.7683384602,-3.0732369101,-0.0847523407
H,0,-2.4127089104,-2.7875872174,-1.7078204814
N,0,-0.859323404,1.3930470188,-0.1644168284
O,0,-0.7654082982,0.5347950202,0.527878874
O,0,-0.8607487592,2.2712593388,-0.8427040669
F,0,3.8433007279,-1.115569146,0.8497293954
B,0,4.4440614192,-0.1661377618,0.0491639631
F,0,5.0321274162,0.7972555033,0.8421092815
F,0,5.4022861636,-0.7665532929,-0.7399416859
F,0,3.4902097205,0.4235649837,-0.7552311094

Pi Complex NO2BF4 PCM ONIOM 3.073_94058
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266217593082

Zero-point correction= 0.157860 (Hartree/Particle)
Thermal correction to Energy= 0.175087
Thermal correction to Enthalpy= 0.176031
Thermal correction to Gibbs Free Energy= 0.105441
Sum of electronic and ZPE= -476.888165
Sum of electronic and thermal Energies= -476.870938
Sum of electronic and thermal Enthalpies= -476.869994
Sum of electronic and thermal Free Energies= -476.940584

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.868 55.709 148.569

C,0,-3.8779930585,-0.8256205229,0.2311964376
C,0,-2.9863934712,-0.5728279453,1.2738685826
C,0,-2.1812471735,0.569207822,1.2526518718
C,0,-2.2516199842,1.4738165105,0.1921100692
C,0,-3.1519152464,1.2072009706,-0.8463370907
C,0,-3.9588829341,0.0736233044,-0.8295902075
C,0,-1.375709831,2.6970344569,0.1462481081
H,0,-4.5111468033,-1.7047280696,0.2550449605
H,0,-2.9267369279,-1.2563806121,2.1142799326
H,0,-1.500045915,0.7595630071,2.0759558062
H,0,-3.2218427244,1.9021132701,-1.6772246208
H,0,-4.6520101554,-0.1071553113,-1.6427282638
H,0,-0.5936114026,2.5839637173,-0.6091554565
H,0,-0.892431365,2.876205139,1.1066771938
H,0,-1.9561560417,3.5827748421,-0.1174674472

N,0,-1.0065765552,-1.706691346,-0.422418877
O,0,-1.1200509319,-0.9738079697,-1.2440391855
O,0,-0.8266502047,-2.4871844589,0.3451982827
F,0,4.7662696235,0.8832484057,-0.7830510159
B,0,3.9710785439,0.075313842,0.0019847883
F,0,3.3961429968,-0.9046243254,-0.7814794135
F,0,4.7367085836,-0.5143006655,0.9859338576
F,0,2.9768849781,0.8335809389,0.5856976874

Pi Complex NO2BF4 PCM ONIOM 3.107_93904
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.277412126795

Zero-point correction= 0.158624 (Hartree/Particle)
Thermal correction to Energy= 0.175113
Thermal correction to Enthalpy= 0.176057
Thermal correction to Gibbs Free Energy= 0.112735
Sum of electronic and ZPE= -476.893161
Sum of electronic and thermal Energies= -476.876672
Sum of electronic and thermal Enthalpies= -476.875728
Sum of electronic and thermal Free Energies= -476.939049

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.885 55.496 133.272

C,0,-2.1878616448,-2.4860625768,0.7280848241
C,0,-1.6380220102,-1.2122254535,0.8595436394
C,0,-1.0656934265,-0.570026181,-0.2466768034
C,0,-1.0398828387,-1.1876886753,-1.4966824157
C,0,-1.5887090376,-2.4702393929,-1.6103089767
C,0,-2.1567271651,-3.1147340739,-0.5143616033
C,0,-0.44549168,-0.5027316984,-2.6977636642
H,0,-2.6090073513,-2.9889206877,1.5934803214
H,0,-1.6507072001,-0.7164699497,1.8253719771
H,0,-0.6524646354,0.4267258236,-0.1317161475
H,0,-1.5685692742,-2.9710174016,-2.5728359031
H,0,-2.5697177475,-4.109827569,-0.62895881
H,0,-1.2122671153,-0.3276079841,-3.455368888
H,0,0.3309315583,-1.1182076491,-3.1567094576
H,0,-0.008999042,0.45934876,-2.4302552079
N,0,0.9043357157,-2.3103486059,0.9783492152
O,0,0.7797794677,-3.0251698201,0.1389285601
O,0,1.1902452659,-1.653385303,1.8291297833
F,0,0.0904237504,-4.3129829587,2.5474293155
B,0,-0.6713534408,-3.9445584768,3.6461024982
F,0,-0.0203706968,-4.3103362346,4.8013877793
F,0,-0.8047136215,-2.5706648827,3.5957045133
F,0,-1.9055821304,-4.5486828089,3.5865467506

Pi Complex NO2BF4 PCM ONIOM 3.137_94117
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.273112150382

Zero-point correction= 0.158058 (Hartree/Particle)
Thermal correction to Energy= 0.174762
Thermal correction to Enthalpy= 0.175706
Thermal correction to Gibbs Free Energy= 0.110625
Sum of electronic and ZPE= -476.893743
Sum of electronic and thermal Energies= -476.877038
Sum of electronic and thermal Enthalpies= -476.876094
Sum of electronic and thermal Free Energies= -476.941175

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.665 55.572 136.975

C,0,5.0182879402,-1.4209373254,-3.5216259863
C,0,5.6357730067,-0.2522877631,-3.0905854836
C,0,5.692859009,0.0512935636,-1.7309230658
C,0,5.1383705619,-0.802736485,-0.7743911138
C,0,4.5167892759,-1.9745908149,-1.2173206336
C,0,4.4562647921,-2.2834310155,-2.5778037159
C,0,5.2081405903,-0.4848616948,0.6945317563
H,0,4.9768201188,-1.6649651231,-4.5761351777
H,0,6.072975203,0.4283443536,-3.8113194422
H,0,6.1734557431,0.9687355348,-1.4081644118
H,0,4.0647667458,-2.6443371292,-0.4886900494
H,0,3.9770120903,-3.2017359596,-2.8999641728
H,0,4.2724087869,-0.7490595009,1.1972634061
H,0,5.4060154915,0.5733368369,0.8650443339
H,0,6.0081857271,-1.0570672599,1.1703438924
N,0,2.1913867355,-0.613867897,-2.4255112214
O,0,2.7283216009,0.3328023135,-2.2192687544
O,0,1.5466508912,-1.4902551112,-2.6490708943
F,0,1.7715185831,-1.111610917,0.1217350758
B,0,1.6196864617,-1.6166818709,1.4045069133
F,0,2.463504437,-2.6914163848,1.5795389225
F,0,1.9091608346,-0.6311695639,2.3226965458
F,0,0.3134498736,-2.0254503863,1.566626177

Pi Complex NO2BF4 PCM ONIOM 3.139_94253
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.273122679758

Zero-point correction= 0.157984 (Hartree/Particle)
Thermal correction to Energy= 0.174740
Thermal correction to Enthalpy= 0.175685
Thermal correction to Gibbs Free Energy= 0.109264
Sum of electronic and ZPE= -476.893819

Sum of electronic and thermal Energies= -476.877063
Sum of electronic and thermal Enthalpies= -476.876118
Sum of electronic and thermal Free Energies= -476.942539

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.651 55.593 139.795

C,0,-3.1804559946,0.4034963697,-0.7960009618
C,0,-1.9577802791,0.3545335062,-1.4690502378
C,0,-0.9840085464,-0.5736427389,-1.0941315133
C,0,-1.2122693228,-1.4686588755,-0.0440316735
C,0,-2.4388288927,-1.4046408946,0.6216876817
C,0,-3.4146989004,-0.4801386035,0.2514593331
C,0,-0.1617316845,-2.4734133604,0.343970515
H,0,-3.937645721,1.1191501966,-1.0922084022
H,0,-1.76442534,1.0340114321,-2.2922612202
H,0,-0.0284035745,-0.59687877,-1.6137977761
H,0,-2.6326245306,-2.0856872258,1.4435422933
H,0,-4.3569157133,-0.4513675739,0.7855571899
H,0,-0.3296845851,-2.8583998627,1.3497442826
H,0,0.8382416036,-2.0300619751,0.303834083
H,0,-0.1720595062,-3.3205905975,-0.3459967995
N,0,-0.7608276865,1.8160468789,0.620523918
O,0,-0.3902113358,2.5527680819,-0.1235337312
O,0,-1.0923919432,1.1656595473,1.4536537791
F,0,3.722527525,0.9550417486,-0.1268884623
B,0,2.7438558186,-0.0070258905,0.0004403664
F,0,1.5629656936,0.608414625,0.388220988
F,0,2.5587510524,-0.6385245965,-1.2097844522
F,0,3.1212078636,-0.9208544215,0.9599658

Pi Complex NO2BF4 PCM ONIOM 3.146_94108
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.273454772103

Zero-point correction= 0.158059 (Hartree/Particle)
Thermal correction to Energy= 0.174823
Thermal correction to Enthalpy= 0.175767
Thermal correction to Gibbs Free Energy= 0.110769
Sum of electronic and ZPE= -476.893790
Sum of electronic and thermal Energies= -476.877026
Sum of electronic and thermal Enthalpies= -476.876082
Sum of electronic and thermal Free Energies= -476.941080

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.703 55.638 136.800

C,0,3.2600129255,0.4714306797,0.6575863815

C,0,2.0723054975,0.4426307223,1.3907724149
C,0,1.0837634238,-0.4995733945,1.0950869655
C,0,1.2649533434,-1.4311893977,0.0675076582
C,0,2.4558998419,-1.3845505066,-0.660961339
C,0,3.4444689892,-0.4446728102,-0.3717468499
C,0,0.2064567731,-2.4581582033,-0.2300118359
H,0,4.0280370767,1.1985603706,0.8912096879
H,0,1.9170514338,1.1493663541,2.1989624156
H,0,0.1549274607,-0.5069955892,1.6616659608
H,0,2.612386753,-2.0929658365,-1.4674467782
H,0,4.3580457592,-0.4305870992,-0.9540279678
H,0,0.3380217755,-2.8901514733,-1.2220114208
H,0,-0.7949938613,-2.0201411615,-0.1722337281
H,0,0.2505077293,-3.2709082653,0.4989332201
N,0,0.7341336936,1.8211017601,-0.6463025512
O,0,0.3424814434,2.538447558,0.1061317846
O,0,1.0806351749,1.1921642608,-1.4900423177
F,0,-3.1397193028,-1.0102696389,-0.8050157135
B,0,-2.7217022125,-0.0361872153,0.0750676387
F,0,-3.7025129285,0.9242550402,0.1978975664
F,0,-2.4635055298,-0.5906646453,1.3096001382
F,0,-1.5708312596,0.5639044909,-0.4136613301

Pi Complex NO2BF4 PCM ONIOM 3.156_94025
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266458589435

Zero-point correction= 0.157694 (Hartree/Particle)
Thermal correction to Energy= 0.174970
Thermal correction to Enthalpy= 0.175914
Thermal correction to Gibbs Free Energy= 0.105613
Sum of electronic and ZPE= -476.888179
Sum of electronic and thermal Energies= -476.870902
Sum of electronic and thermal Enthalpies= -476.869958
Sum of electronic and thermal Free Energies= -476.940259

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.795 55.767 147.961

C,0,-3.8286256057,-1.0717485555,0.5317084246
C,0,-2.8063394345,-0.6643613314,1.3862858981
C,0,-2.1779349681,0.5714005994,1.1966401776
C,0,-2.5622370431,1.418446949,0.156100551
C,0,-3.5853643642,0.9917769341,-0.698351804
C,0,-4.2141547574,-0.2365167485,-0.5146869459
C,0,-1.9068942629,2.7583690761,-0.0460774731
H,0,-4.3210132369,-2.0247654287,0.6841026661
H,0,-2.5026784815,-1.2991908607,2.2119215347
H,0,-1.3917652243,0.8823686331,1.8777845898

H,0,-3.8943834114,1.6343968419,-1.5168198559
H,0,-5.0063112085,-0.5418367025,-1.1882911688
H,0,-1.0991685154,2.9171627302,0.668453788
H,0,-2.6344266507,3.562937556,0.081444894
H,0,-1.4968916232,2.8475854189,-1.0543694714
N,0,-0.8924491138,-1.4441912171,-0.5642783356
O,0,-0.3284913612,-1.9875726913,0.2215375758
O,0,-1.3925654215,-0.9470835365,-1.417745049
F,0,3.3900829405,0.8565743383,-0.8210226437
B,0,4.1909037352,0.0561712721,-0.0319336496
F,0,3.4067931902,-0.8801356436,0.6102791324
F,0,5.1176137027,-0.5876239291,-0.8247885631
F,0,4.8393301157,0.8337232959,0.9041357278

Pi Complex NO2BF4 PCM ONIOM 3.158_94252
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.274019242422

Zero-point correction= 0.157750 (Hartree/Particle)
Thermal correction to Energy= 0.174762
Thermal correction to Enthalpy= 0.175706
Thermal correction to Gibbs Free Energy= 0.108400
Sum of electronic and ZPE= -476.893170
Sum of electronic and thermal Energies= -476.876158
Sum of electronic and thermal Enthalpies= -476.875214
Sum of electronic and thermal Free Energies= -476.942520

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.665 55.749 141.658

C,0,4.1718200974,-2.594843568,-0.5969244901
C,0,4.3367997138,-2.3027378673,-1.9493980158
C,0,4.9162959726,-1.0992039473,-2.3420336363
C,0,5.3435167515,-0.157987826,-1.3992286139
C,0,5.1649240456,-0.4545243179,-0.0472976975
C,0,4.5859173502,-1.6655673053,0.354089587
C,0,5.9893496011,1.1287325058,-1.8387907356
H,0,3.6983468484,-3.5216836419,-0.2872155679
H,0,4.0080629513,-3.0116433557,-2.7001697484
H,0,5.0382617035,-0.8841909453,-3.3986638245
H,0,5.493456896,0.2558151655,0.7046620184
H,0,4.464387305,-1.8794619657,1.4105334537
H,0,6.9789644918,0.9346068905,-2.2585282971
H,0,6.1093292894,1.8189929351,-1.0037013576
H,0,5.3983562272,1.6215119655,-2.6130485362
N,0,2.2899375255,-0.106186477,-0.1038336358
O,0,2.2542580638,-0.2730219572,-1.1986009723
O,0,2.207003002,0.1312987495,0.9784701229
F,0,1.5843783728,-4.6749204894,0.7067101965

B,0,0.7751224777,-3.7358431416,0.1059847184
F,0,0.7787948061,-3.9194130454,-1.2595674781
F,0,-0.5104334053,-3.8535969825,0.5866614189
F,0,1.2464162123,-2.4630433782,0.3931486914

Pi Complex NO2BF4 PCM ONIOM 3.163_93717
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267265488654

Zero-point correction= 0.158040 (Hartree/Particle)
Thermal correction to Energy= 0.174925
Thermal correction to Enthalpy= 0.175869
Thermal correction to Gibbs Free Energy= 0.109640
Sum of electronic and ZPE= -476.888774
Sum of electronic and thermal Energies= -476.871889
Sum of electronic and thermal Enthalpies= -476.870945
Sum of electronic and thermal Free Energies= -476.937174

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.767 55.594 139.390

C,0,5.1918020863,0.2016578552,4.7005408337
C,0,4.7922987579,-0.5202539425,5.8221055054
C,0,4.1441401872,-1.7435408854,5.67353596
C,0,3.880590687,-2.2758302417,4.4070212618
C,0,4.2751056781,-1.5394461871,3.2879470816
C,0,4.9288038206,-0.3109684585,3.4315356011
C,0,3.2092375867,-3.6150611649,4.2644666277
H,0,5.7045645256,1.149381959,4.8113226943
H,0,4.9859324422,-0.1312594792,6.814837323
H,0,3.8384107794,-2.2973703615,6.5554874762
H,0,4.0823284193,-1.933340159,2.2910856008
H,0,5.2423201008,0.235284327,2.5480952508
H,0,3.9068790086,-4.4167305606,4.5183726005
H,0,2.8667755325,-3.7830503071,3.2424968156
H,0,2.3535102544,-3.7021483556,4.9361455988
N,0,2.2363021095,0.5475089329,3.6276885156
O,0,2.0793276831,0.1792273382,4.6602616509
O,0,2.2908012498,0.9733940488,2.6043799776
F,0,3.6316670952,-1.62331694,-0.2358570831
B,0,2.5847909883,-2.5039249684,-0.4135961874
F,0,2.8609765951,-3.3419141225,-1.4733630707
F,0,2.4074008407,-3.252627007,0.7316128159
F,0,1.4297908717,-1.7936835199,-0.6722592502

Pi Complex NO2BF4 PCM ONIOM 3.173_93824
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.277777528472

Zero-point correction= 0.159150 (Hartree/Particle)
Thermal correction to Energy= 0.175184
Thermal correction to Enthalpy= 0.176128
Thermal correction to Gibbs Free Energy= 0.114528
Sum of electronic and ZPE= -476.893626
Sum of electronic and thermal Energies= -476.877592
Sum of electronic and thermal Enthalpies= -476.876648
Sum of electronic and thermal Free Energies= -476.938248

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.930 55.079 129.648

C,0,3.2249727939,0.6106217002,0.4981049261
C,0,2.1432100674,0.5198141093,1.3739561707
C,0,1.1741981404,-0.4733359014,1.1957152533
C,0,1.2672192735,-1.392947329,0.1442048863
C,0,2.3489692521,-1.277910989,-0.7306631169
C,0,3.3188717661,-0.2885337244,-0.5573706205
C,0,0.226950564,-2.4656661738,-0.0204686392
H,0,3.9802632937,1.3734967293,0.6404285115
H,0,2.0567024126,1.2107167536,2.2054377206
H,0,0.3366788402,-0.5368675446,1.8864103441
H,0,2.4382305238,-1.9718817829,-1.5594483119
H,0,4.1480547219,-0.2248753718,-1.2518227443
H,0,0.2464035575,-3.1480030202,0.8319296748
H,0,0.3991947509,-3.0494057994,-0.9239561902
H,0,-0.7952454084,-2.0388325603,-0.0714509433
N,0,0.4100984136,1.7173159396,-0.4615382456
O,0,0.8576782118,1.2427880425,-1.3591437285
O,0,-0.1006393355,2.3089013498,0.3299776321
F,0,-1.9889360723,0.3755662734,1.0966337253
B,0,-2.5618730862,-0.0978933976,-0.0665708647
F,0,-2.4996082611,-1.474810207,-0.0937571456
F,0,-3.8661574113,0.3248137697,-0.1617672891
F,0,-1.8198610086,0.4172551338,-1.1180190049

Pi Complex NO2BF4 PCM ONIOM 3.178_94087
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.273688937032

Zero-point correction= 0.158196 (Hartree/Particle)
Thermal correction to Energy= 0.174943
Thermal correction to Enthalpy= 0.175887
Thermal correction to Gibbs Free Energy= 0.110731
Sum of electronic and ZPE= -476.893405
Sum of electronic and thermal Energies= -476.876658
Sum of electronic and thermal Enthalpies= -476.875714
Sum of electronic and thermal Free Energies= -476.940870

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.778 55.635 137.132

C,0,3.4970237463,-0.408405004,0.1215216464
C,0,3.3011343492,0.5403826174,-0.8758151655
C,0,2.2290987481,1.4301156495,-0.7997993414
C,0,1.3320349676,1.3942504619,0.2694518568
C,0,1.5297496144,0.4269997136,1.2616169383
C,0,2.6032276889,-0.4662854092,1.1908969238
C,0,0.1758359302,2.3541107512,0.3522774846
H,0,4.3347423175,-1.0931569802,0.0726017169
H,0,3.9837146618,0.5936930059,-1.7156720056
H,0,2.091502558,2.1677990119,-1.5831558254
H,0,0.8491631931,0.3818148538,2.1068901459
H,0,2.7477875109,-1.1953187422,1.9808829872
H,0,-0.7762906711,1.8400217257,0.1761328408
H,0,0.2689024687,3.1484241848,-0.3879856944
H,0,0.1186207948,2.8109165055,1.3416494384
N,0,0.6847434024,-1.7998395751,-0.3851206351
O,0,0.8834523865,-1.2220111108,-1.309513621
O,0,0.4199605311,-2.4687137201,0.461953952
F,0,-2.970646463,0.7030262893,1.1526077817
B,0,-2.8535196673,0.0473363501,-0.0531773063
F,0,-3.8666661762,-0.878676202,-0.1757305888
F,0,-2.9243442381,0.9509493848,-1.0907209634
F,0,-1.6360266536,-0.6149067617,-0.104121566

Pi Complex NO2BF4 PCM ONIOM 3.180_94194
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266022363459

Zero-point correction= 0.157283 (Hartree/Particle)
Thermal correction to Energy= 0.174761
Thermal correction to Enthalpy= 0.175705
Thermal correction to Gibbs Free Energy= 0.103846
Sum of electronic and ZPE= -476.888506
Sum of electronic and thermal Energies= -476.871028
Sum of electronic and thermal Enthalpies= -476.870084
Sum of electronic and thermal Free Energies= -476.941943

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.664 55.856 151.241

C,0,3.2793401828,1.843435976,-0.2963201075
C,0,3.2413519392,1.2508368027,0.9636489244
C,0,3.4767911822,-0.1213436599,1.1058495071
C,0,3.7599594409,-0.9189596185,-0.0043123763
C,0,3.7879902268,-0.3098797079,-1.263909985

C,0,3.5514369435,1.0539367256,-1.4117208348
C,0,4.040564773,-2.3909036454,0.1381386949
H,0,3.1026541095,2.9067456844,-0.4063685732
H,0,3.0391257862,1.8544337917,1.8422862044
H,0,3.4555982618,-0.5672309729,2.0954140786
H,0,4.0023254824,-0.9145541396,-2.1396790097
H,0,3.5808396779,1.5005493178,-2.3988026221
H,0,5.0829296902,-2.6062137709,-0.1078915585
H,0,3.418244626,-2.9778649233,-0.5403997362
H,0,3.8577694218,-2.7348536667,1.156256977
N,0,0.629542051,0.2393373097,0.4260075238
O,0,0.8528237814,-0.0748260822,-0.6115937913
O,0,0.3079423207,0.5324042327,1.4467050095
F,0,-5.6842482499,0.5367605657,0.6650256251
B,0,-4.7404756353,-0.098486184,-0.1141805268
F,0,-3.9468492646,-0.8960927845,0.6847809428
F,0,-5.3684379448,-0.8791339917,-1.0618290723
F,0,-3.9532808027,0.8440307414,-0.743776294

Pi Complex NO2BF4 PCM ONIOM 3.191_93775
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267820774694

Zero-point correction= 0.157848 (Hartree/Particle)
Thermal correction to Energy= 0.174765
Thermal correction to Enthalpy= 0.175709
Thermal correction to Gibbs Free Energy= 0.109175
Sum of electronic and ZPE= -476.889080
Sum of electronic and thermal Energies= -476.872163
Sum of electronic and thermal Enthalpies= -476.871219
Sum of electronic and thermal Free Energies= -476.937753

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.666 55.637 140.032

C,0,2.8532320606,0.4448279652,4.0773677583
C,0,2.1013665111,0.4002018353,5.2484884314
C,0,1.1257201115,-0.5787724657,5.4190475367
C,0,0.8777435004,-1.5355002076,4.4294220503
C,0,1.627526897,-1.4748035196,3.2528686516
C,0,2.6110774947,-0.4943821751,3.0774307926
C,0,-0.1580124697,-2.6067055752,4.6412929432
H,0,3.6195045693,1.1989995166,3.9456536626
H,0,2.2742960876,1.1283813264,6.0320377523
H,0,0.5467639172,-0.6035519213,6.3367318381
H,0,1.4508523682,-2.2067296409,2.4655630865
H,0,3.1940319634,-0.4781087305,2.1625988127
H,0,0.1958194278,-3.336607254,5.3731249162
H,0,-0.374039181,-3.14078359,3.7146519582

H,0,-1.0893770955,-2.1856945614,5.0239929131
N,0,0.289534126,0.8876886367,2.2290103188
O,0,-0.0627687741,1.1318896101,3.2502898498
O,0,0.5583110853,0.7253729805,1.1643648547
F,0,1.3461197076,-2.7656092609,-0.0413313397
B,0,0.336572365,-3.6907108575,0.1297403817
F,0,0.8790456899,-4.8974604315,0.5183942171
F,0,-0.5453908892,-3.2455896697,1.0934625038
F,0,-0.338748673,-3.8492043101,-1.0629855898

Pi Complex NO2BF4 PCM ONIOM 3.208_93983
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.274697447668

Zero-point correction= 0.158304 (Hartree/Particle)
Thermal correction to Energy= 0.175013
Thermal correction to Enthalpy= 0.175957
Thermal correction to Gibbs Free Energy= 0.111385
Sum of electronic and ZPE= -476.892915
Sum of electronic and thermal Energies= -476.876205
Sum of electronic and thermal Enthalpies= -476.875261
Sum of electronic and thermal Free Energies= -476.939833

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.822 55.625 135.903

C,0,0.4263675733,1.3793791248,0.4081483167
C,0,0.9003036984,0.4351528431,1.313955792
C,0,2.1917812415,-0.0914387456,1.1736898623
C,0,3.0278411385,0.322465029,0.1350311165
C,0,2.5336761747,1.2675675471,-0.7699780058
C,0,1.249370096,1.7896055456,-0.6392355063
C,0,4.4227625054,-0.223929362,-0.0127658127
H,0,-0.5853838986,1.7636952448,0.5010374425
H,0,0.2673293015,0.1025620551,2.1298746591
H,0,2.553096842,-0.8195903319,1.8932422964
H,0,3.1638895989,1.5960224972,-1.5900278933
H,0,0.8878518485,2.5147975481,-1.358784896
H,0,4.6274550043,-0.9946391239,0.730320957
H,0,5.1609350118,0.5709864053,0.1120051792
H,0,4.572528393,-0.6542816204,-1.0051813276
N,0,0.5588023242,-1.693041805,-0.5072027037
O,0,0.7228305098,-1.0704376945,-1.4093790108
O,0,0.355907778,-2.4285438025,0.3012820698
F,0,-2.8933881639,0.704355874,1.3314938947
B,0,-2.9129206203,0.1543225446,0.0688140694
F,0,-2.8399434709,1.1517452755,-0.8788332191
F,0,-1.8302826319,-0.6997389751,-0.0830365153
F,0,-4.0743752545,-0.5658460734,-0.1055587651

Pi Complex NO2BF4 PCM ONIOM 3.215_94153
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266546634745

Zero-point correction= 0.157705 (Hartree/Particle)
Thermal correction to Energy= 0.175147
Thermal correction to Enthalpy= 0.176092
Thermal correction to Gibbs Free Energy= 0.104203
Sum of electronic and ZPE= -476.888028
Sum of electronic and thermal Energies= -476.870585
Sum of electronic and thermal Enthalpies= -476.869641
Sum of electronic and thermal Free Energies= -476.941530

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.907 55.760 151.303

C,0,1.7667138673,-1.7776005941,-1.8406867687
C,0,1.454153846,-0.6217503128,-2.5483969888
C,0,2.1720705834,0.5542152192,-2.328300094
C,0,3.2147127536,0.601718855,-1.4011433604
C,0,3.5143104509,-0.5640675564,-0.6864327707
C,0,2.8006740469,-1.7447755978,-0.9043984542
C,0,4.0066164531,1.8617366238,-1.1724610728
H,0,1.2166101894,-2.6943306435,-2.0157858251
H,0,0.6508424821,-0.6319540961,-3.276015235
H,0,1.9178732958,1.4479213856,-2.8887203998
H,0,4.3265665969,-0.5530726306,0.0348583934
H,0,3.0631447832,-2.6409753677,-0.3520688319
H,0,5.0576238554,1.704621843,-1.4242640982
H,0,3.9659838417,2.1692867826,-0.1251461504
H,0,3.6306392233,2.6821563249,-1.7833348315
N,0,1.1286637019,-0.4062653282,0.9971246387
O,0,0.6202862596,0.2157361719,0.2356698865
O,0,1.5648688438,-1.0023460783,1.8251391562
F,0,2.0991684405,4.5455461087,4.7545834585
B,0,1.0431410037,3.7582421559,4.3466079726
F,0,-0.111350009,4.1611736064,4.9841444497
F,0,0.879650548,3.8773591895,2.9815216822
F,0,1.3048763427,2.4400187393,4.6601323439

Pi Complex NO2BF4 PCM ONIOM 3.217_93889
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267250548074

Zero-point correction= 0.158048 (Hartree/Particle)
Thermal correction to Energy= 0.175237
Thermal correction to Enthalpy= 0.176182
Thermal correction to Gibbs Free Energy= 0.107389

Sum of electronic and ZPE= -476.888234
Sum of electronic and thermal Energies= -476.871044
Sum of electronic and thermal Enthalpies= -476.870100
Sum of electronic and thermal Free Energies= -476.938893

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.963 55.726 144.787

C,0,3.9573147694,0.3105720139,-0.4117434382
C,0,3.4085395912,0.4008987591,0.8650621716
C,0,2.3442508144,-0.4291810822,1.2351414906
C,0,1.8154566312,-1.3631679025,0.3400639443
C,0,2.3724605846,-1.4348457965,-0.9405427705
C,0,3.4306002318,-0.6096280462,-1.3149010747
C,0,0.666503938,-2.2535774728,0.7310878586
H,0,4.7885636861,0.944626342,-0.6955291545
H,0,3.8159507229,1.1034695508,1.584271759
H,0,1.9363792112,-0.3603213799,2.239372099
H,0,1.9746738124,-2.1511213369,-1.6524764027
H,0,3.8471970088,-0.6900241458,-2.3122294732
H,0,0.5783801293,-2.3338527753,1.8147393928
H,0,0.7921736385,-3.2561800911,0.3205038367
H,0,-0.2803101313,-1.8608481097,0.3474908115
N,0,1.1546015354,1.8540072819,-0.0750040898
O,0,1.1251466132,2.4596741672,0.8546243085
O,0,1.1172749761,1.3260836963,-1.0474004351
F,0,-4.4065313782,0.5784227715,0.9399819586
B,0,-3.6635255909,-0.0932647771,-0.0082741881
F,0,-2.6334133261,-0.769174717,0.6129415869
F,0,-4.4677628313,-0.9908888404,-0.6781200799
F,0,-3.1380936368,0.8147908907,-0.9049321112

Pi Complex NO2BF4 PCM ONIOM 3.221_94009
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266867901234

Zero-point correction= 0.157916 (Hartree/Particle)
Thermal correction to Energy= 0.175144
Thermal correction to Enthalpy= 0.176088
Thermal correction to Gibbs Free Energy= 0.105776
Sum of electronic and ZPE= -476.887953
Sum of electronic and thermal Energies= -476.870726
Sum of electronic and thermal Enthalpies= -476.869781
Sum of electronic and thermal Free Energies= -476.940093

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.904 55.720 147.984

C,0,1.5556200145,1.5754920445,-0.6853394126
C,0,2.2885925767,1.8845290006,0.4584182486
C,0,3.4035202248,1.1246461114,0.8039489733
C,0,3.8137822317,0.0417810676,0.0196504476
C,0,3.0629124392,-0.2696272045,-1.1161963398
C,0,1.9440845708,0.4934085604,-1.4710206975
C,0,5.0443752106,-0.745350419,0.3831464923
H,0,0.6917041497,2.1688271397,-0.960954445
H,0,1.9922460109,2.7194385956,1.082783305
H,0,3.9673818441,1.3773827577,1.6962879107
H,0,3.3629110219,-1.1026773309,-1.744534854
H,0,1.387101458,0.2453206289,-2.3685508735
H,0,5.0759143577,-0.9584561118,1.4529682743
H,0,5.9438860758,-0.1762436186,0.1361840505
H,0,5.0882929006,-1.6896064109,-0.1597713464
N,0,0.8295056288,-1.3782347092,0.3754504086
O,0,1.0977485007,-0.780467718,1.2677298019
O,0,0.504210927,-2.0431241616,-0.4513467486
F,0,-3.6499683631,-1.1474448116,0.1808504607
B,0,-4.1669717354,0.1239860612,0.0367555536
F,0,-3.2997069352,0.8853074252,-0.7200148348
F,0,-5.390903833,0.0569049809,-0.5944631797
F,0,-4.3159212767,0.7016051225,1.2805278047

Pi Complex NO2BF4 PCM ONIOM 3.228_94053
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266407337192

Zero-point correction= 0.157742 (Hartree/Particle)
Thermal correction to Energy= 0.175043
Thermal correction to Enthalpy= 0.175987
Thermal correction to Gibbs Free Energy= 0.105306
Sum of electronic and ZPE= -476.888101
Sum of electronic and thermal Energies= -476.870800
Sum of electronic and thermal Enthalpies= -476.869856
Sum of electronic and thermal Free Energies= -476.940537

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	109.841	55.741	148.762

C,0,-3.8554348654,-1.319479151,0.7528593789
C,0,-3.683802956,-0.2533884912,1.6314693819
C,0,-3.2942383309,0.9964082371,1.1532643784
C,0,-3.0698843008,1.2122783263,-0.2094069071
C,0,-3.2330580933,0.1323809303,-1.0817481623
C,0,-3.6261023494,-1.1235309806,-0.607615228
C,0,-2.693732763,2.5755033174,-0.7252762244

H,0,-4.1647478832,-2.2901854963,1.1211624208
H,0,-3.8518754441,-0.3934754841,2.6929986154
H,0,-3.1633546307,1.817883813,1.8502107839
H,0,-3.0693128072,0.2759034287,-2.1457400671
H,0,-3.7624407884,-1.9416077464,-1.3067614789
H,0,-2.1310959935,3.1400262077,0.0191199557
H,0,-3.592844516,3.1491030661,-0.9645051604
H,0,-2.0956986387,2.5082577595,-1.6349710016
N,0,-0.7855192093,-1.1939381069,-0.239702394
O,0,-0.821527899,-0.6796788283,0.7397170216
O,0,-0.6501427327,-1.7334561813,-1.2000041987
F,0,3.8093518314,-0.7375386913,0.8116876664
B,0,4.4024370157,0.20542164,-0.002731959
F,0,5.1999724022,1.0339428208,0.7580759804
F,0,5.1697952821,-0.4298154497,-0.9564827276
F,0,3.4232256702,0.9526860601,-0.6247460743

Pi Complex NO2BF4 PCM ONIOM 3.229_94135
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266475122039

Zero-point correction= 0.157610 (Hartree/Particle)
Thermal correction to Energy= 0.174953
Thermal correction to Enthalpy= 0.175897
Thermal correction to Gibbs Free Energy= 0.104442
Sum of electronic and ZPE= -476.888188
Sum of electronic and thermal Energies= -476.870845
Sum of electronic and thermal Enthalpies= -476.869900
Sum of electronic and thermal Free Energies= -476.941356

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.785 55.760 150.391

C,0,3.8290616878,1.2862642092,0.7403010871
C,0,3.6556969672,0.2112530925,1.6090959098
C,0,3.2542456857,-1.0294460271,1.1202124837
C,0,3.0188763256,-1.2290394202,-0.2441269889
C,0,3.1845080737,-0.1419944302,-1.1053711716
C,0,3.5897476368,1.1068080015,-0.6197986869
C,0,2.6207125214,-2.5851163054,-0.7624478612
H,0,4.1483199766,2.250468532,1.1171144396
H,0,3.832443132,0.3387929473,2.6707950717
H,0,3.1221890095,-1.8583725486,1.8083153164
H,0,3.0135829458,-0.2720411213,-2.1698119245
H,0,3.7280819475,1.9310292886,-1.3112672362
H,0,2.2187450046,-2.5240881837,-1.7740198852
H,0,1.8716183659,-3.0492686735,-0.1186108146
H,0,3.4875900321,-3.2499236808,-0.7872927507
N,0,0.751337557,1.1893213836,-0.2334896118

O,0,0.6126477764,1.7384936124,-1.1878115516
O,0,0.791163245,0.6655857726,0.7407946193
F,0,-4.6702668486,0.6815154968,-1.0107767842
B,0,-4.3664886314,-0.1733952347,0.0285124107
F,0,-5.5032343577,-0.843181253,0.428558444
F,0,-3.4185751958,-1.0845807995,-0.3904883968
F,0,-3.862040857,0.5554033415,1.0862538819

Pi Complex NO2BF4 PCM ONIOM 3.231_94060
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266441526657

Zero-point correction= 0.157613 (Hartree/Particle)
Thermal correction to Energy= 0.174934
Thermal correction to Enthalpy= 0.175878
Thermal correction to Gibbs Free Energy= 0.105230
Sum of electronic and ZPE= -476.888221
Sum of electronic and thermal Energies= -476.870900
Sum of electronic and thermal Enthalpies= -476.869956
Sum of electronic and thermal Free Energies= -476.940605

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.773 55.769 148.692

C,0,-0.4190673236,-0.1108187938,3.5945498909
C,0,-1.1910501841,0.9931804677,3.2417311196
C,0,-2.0046615008,0.9495465567,2.1034512529
C,0,-2.0644732225,-0.1955043973,1.3058453305
C,0,-1.2754638996,-1.2920181534,1.6687270873
C,0,-0.4629647818,-1.2535851796,2.7991746575
C,0,-2.9656023303,-0.2649712243,0.1019826841
H,0,0.2066346888,-0.0810026813,4.4784182674
H,0,-1.1747355395,1.8883366003,3.8541611474
H,0,-2.6115625871,1.8126064369,1.8465825376
H,0,-1.2994132359,-2.1885771208,1.0574572161
H,0,0.1377325818,-2.1176424905,3.0585704113
H,0,-3.8533350284,-0.8606935626,0.3280341365
H,0,-2.4608511745,-0.7383754753,-0.7419465829
H,0,-3.299227505,0.7264502406,-0.2052220996
N,0,0.6279916602,1.7325435076,1.1557602803
O,0,0.4711624784,2.8107100778,1.3666005118
O,0,0.8660858793,0.6854776627,0.8871317533
F,0,2.1202774106,1.5080041391,-3.4060068236
B,0,2.7954293645,2.6846856784,-3.6584368345
F,0,2.4668849635,3.1433086,-4.9165801119
F,0,2.4367500024,3.6269443783,-2.716116763
F,0,4.1541583838,2.4592218327,-3.5856359692

Pi Complex NO2BF4 PCM ONIOM 3.236_93860

ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266421809273

Zero-point correction= 0.157946 (Hartree/Particle)
Thermal correction to Energy= 0.175144
Thermal correction to Enthalpy= 0.176088
Thermal correction to Gibbs Free Energy= 0.107281
Sum of electronic and ZPE= -476.887940
Sum of electronic and thermal Energies= -476.870742
Sum of electronic and thermal Enthalpies= -476.869798
Sum of electronic and thermal Free Energies= -476.938605

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.904 55.721 144.817

C,0,-1.0520848413,4.0552926138,1.3748907602
C,0,-1.6201718748,2.8192832659,1.6705779456
C,0,-0.8678613864,1.6467609733,1.5320526119
C,0,0.4612135406,1.6917948672,1.1040015183
C,0,1.0133745016,2.9409912383,0.8017246326
C,0,0.2689583863,4.110049239,0.9346709543
C,0,1.2835802159,0.4391645219,0.9609807737
H,0,-1.6298736599,4.9644069355,1.4896143906
H,0,-2.6434408831,2.7615216472,2.0263576274
H,0,-1.3170413041,0.6905822987,1.7831951761
H,0,2.0430923986,2.9968954344,0.4625381449
H,0,0.7223812511,5.0653577612,0.6972585031
H,0,0.7693312762,-0.4247775538,1.3817373905
H,0,2.2431601664,0.5470408534,1.469679154
H,0,1.4966597485,0.2274835288,-0.0908620601
N,0,-1.9778566204,2.1866716248,-1.0997378456
O,0,-2.9340730768,1.6650537189,-0.8878720585
O,0,-1.0526526175,2.7077309305,-1.4125059007
F,0,-0.1563406008,-1.9412388022,-4.1168122754
B,0,0.74116532,-2.0827322744,-3.0783366183
F,0,0.7103774606,-0.9489432756,-2.2926850151
F,0,0.3959741312,-3.1799770832,-2.3172504464
F,0,2.010840368,-2.2549157637,-3.5887311632

Pi Complex NO2BF4 PCM ONIOM 3.237_93813
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267722282933

Zero-point correction= 0.157963 (Hartree/Particle)
Thermal correction to Energy= 0.175049
Thermal correction to Enthalpy= 0.175993
Thermal correction to Gibbs Free Energy= 0.108305
Sum of electronic and ZPE= -476.888476
Sum of electronic and thermal Energies= -476.871391

Sum of electronic and thermal Enthalpies= -476.870447
Sum of electronic and thermal Free Energies= -476.938134

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.845 55.627 142.461

C,0,0.6663989496,-1.3513628322,-0.2853246724
C,0,1.8549539536,-1.7321199654,-0.9037473934
C,0,3.0743952811,-1.2359593787,-0.4481391532
C,0,3.138174701,-0.351966005,0.6327837553
C,0,1.9391925505,0.0350633139,1.237397559
C,0,0.7113760922,-0.4635521206,0.7862299477
C,0,4.4644135666,0.1452774289,1.1424084244
H,0,-0.2867139583,-1.7353304325,-0.633748589
H,0,1.8337520494,-2.4167454503,-1.7436452761
H,0,3.9930606829,-1.5425277416,-0.9377770501
H,0,1.9610753753,0.7162920932,2.0826933331
H,0,-0.208412204,-0.1610242721,1.2791811411
H,0,4.9431079174,-0.6191513964,1.7592813552
H,0,4.3464656687,1.039761477,1.7547055536
H,0,5.1438704715,0.3744761654,0.3201189102
N,0,1.1914638367,1.7840228637,-0.8996660064
O,0,1.7262247773,1.1811950007,-1.659367728
O,0,0.6536187486,2.4790755745,-0.2215541965
F,0,-4.330804864,-0.9166815279,0.8657521579
B,0,-3.5359642363,-0.2386710254,-0.0341219849
F,0,-2.6384814015,0.5558792677,0.6493863525
F,0,-2.85104459,-1.1440903116,-0.8181310962
F,0,-4.3239253685,0.5574842749,-0.839726344

Pi Complex NO2BF4 PCM ONIOM 3.238_93914
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267135462019

Zero-point correction= 0.157588 (Hartree/Particle)
Thermal correction to Energy= 0.174781
Thermal correction to Enthalpy= 0.175725
Thermal correction to Gibbs Free Energy= 0.107245
Sum of electronic and ZPE= -476.888804
Sum of electronic and thermal Energies= -476.871611
Sum of electronic and thermal Enthalpies= -476.870667
Sum of electronic and thermal Free Energies= -476.939147

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.677 55.766 144.129

C,0,0.4274386204,-1.1069622223,-0.1144211646
C,0,0.9577926224,-0.3352574582,-1.1443932856

C,0,2.3365310801,-0.1028282145,-1.2128891135
C,0,3.2045754605,-0.6419382662,-0.2593031274
C,0,2.6538535471,-1.4035467714,0.7753252289
C,0,1.2823593516,-1.6360170943,0.8495887154
C,0,4.6927518475,-0.4385900538,-0.356285357
H,0,-0.643832679,-1.2783205509,-0.0598823284
H,0,0.3009444366,0.0798136111,-1.9020399449
H,0,2.7397278156,0.4877070569,-2.0301861094
H,0,3.3098572333,-1.8222843551,1.5315973516
H,0,0.8810376736,-2.2298577825,1.6625786213
H,0,4.9396084406,0.4132247572,-0.9903176111
H,0,5.1659290916,-1.3231860665,-0.7896856204
H,0,5.1360182387,-0.2797218654,0.6279839958
N,0,1.332634257,1.9331701445,0.5382230464
O,0,1.4674108948,1.313139337,1.4456931796
O,0,1.1899401716,2.6517877823,-0.2958661866
F,0,-2.983209786,-0.88747786,0.9444091191
B,0,-3.550858468,-0.1302129195,-0.0595812832
F,0,-4.3575203034,-0.930408263,-0.8409365738
F,0,-4.3057471295,0.8785556281,0.5034433632
F,0,-2.560128417,0.4275164267,-0.8414599153

Pi Complex NO2BF4 PCM ONIOM 3.242_93631
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.276080899456

Zero-point correction= 0.158860 (Hartree/Particle)
Thermal correction to Energy= 0.175272
Thermal correction to Enthalpy= 0.176216
Thermal correction to Gibbs Free Energy= 0.113061
Sum of electronic and ZPE= -476.890517
Sum of electronic and thermal Energies= -476.874105
Sum of electronic and thermal Enthalpies= -476.873161
Sum of electronic and thermal Free Energies= -476.936316

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.985 55.421 132.920

C,0,-0.5245200261,0.0170458747,3.6629926804
C,0,-0.6344555357,1.211088942,2.9540499914
C,0,-1.8619322273,1.6054477412,2.4255641138
C,0,-3.0072673517,0.8225136516,2.59109031
C,0,-2.8828136823,-0.3839696236,3.2861081311
C,0,-1.6515852678,-0.7831316939,3.8246792482
C,0,-4.334940906,1.2835765865,2.0525581942
H,0,0.4296967289,-0.3019616237,4.065202145
H,0,0.2379896218,1.8370362079,2.8088457663
H,0,-1.9324907692,2.5377743775,1.8751148836
H,0,-3.7557124873,-1.014312225,3.4257982241

H,0,-1.5720468917,-1.7309121195,4.3521981111
H,0,-4.7419262857,2.0772850766,2.6835580394
H,0,-5.0615755834,0.4714261142,2.0283165174
H,0,-4.2326002897,1.6884473056,1.0443849349
N,0,-1.6349317234,-1.7218758998,1.1610963777
O,0,-2.1672128407,-2.6723129423,1.3798029591
O,0,-1.062460227,-0.8429176748,0.7931148475
F,0,-1.2557412541,-3.9559135114,2.78663395
B,0,0.0838516166,-3.8351287792,3.1138925087
F,0,0.5373701309,-2.6927502968,2.4732114485
F,0,0.2276440327,-3.7083541248,4.4754533965
F,0,0.7808738183,-4.9301917627,2.6606032213

Pi Complex NO2BF4 PCM ONIOM 3.245_94016
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.272037025824

Zero-point correction= 0.157778 (Hartree/Particle)
Thermal correction to Energy= 0.174707
Thermal correction to Enthalpy= 0.175651
Thermal correction to Gibbs Free Energy= 0.108993
Sum of electronic and ZPE= -476.891383
Sum of electronic and thermal Energies= -476.874454
Sum of electronic and thermal Enthalpies= -476.873510
Sum of electronic and thermal Free Energies= -476.940168

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.630 55.753 140.294

C,0,2.2781453036,3.569273213,-0.4487834135
C,0,1.4978144028,3.3774687387,0.6894590925
C,0,1.8749037338,2.4431162331,1.650800787
C,0,3.0361101845,1.6783666974,1.5014217943
C,0,3.8059670989,1.871176341,0.3518356553
C,0,3.4331830179,2.8112214751,-0.6168205334
C,0,3.4256393111,0.6668908051,2.5462941689
H,0,1.9911515382,4.3012848399,-1.1939093438
H,0,0.5934202372,3.9577952027,0.8306916252
H,0,1.2590852613,2.3040596917,2.5337765819
H,0,4.717397147,1.2966616568,0.215769742
H,0,4.0579743954,2.9567187252,-1.4916189805
H,0,4.435094453,0.2907727615,2.3795772085
H,0,2.7407613352,-0.1851358985,2.5369750748
H,0,3.3835498743,1.1057228171,3.5445518115
N,0,1.9539530669,0.4650841757,-1.3385892038
O,0,2.7537869887,0.115489489,-2.0253908819
O,0,1.0886367047,0.7421071387,-0.7050807568
F,0,0.4407055041,-3.907431084,-2.4398577643
B,0,0.7954792373,-3.3596021189,-1.2267926384

F,0,0.9683053184,-1.9934626807,-1.3793249474
F,0,-0.197083883,-3.5923463717,-0.3001326903
F,0,1.9775047685,-3.9168295479,-0.7893171877

Pi Complex NO2BF4 PCM ONIOM 3.247_94177
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266265816368

Zero-point correction= 0.157332 (Hartree/Particle)
Thermal correction to Energy= 0.174759
Thermal correction to Enthalpy= 0.175704
Thermal correction to Gibbs Free Energy= 0.103994
Sum of electronic and ZPE= -476.888438
Sum of electronic and thermal Energies= -476.871011
Sum of electronic and thermal Enthalpies= -476.870067
Sum of electronic and thermal Free Energies= -476.941777

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.663 55.860 150.926

C,0,-0.3822921097,-1.721830326,-3.2582543068
C,0,-0.6183366755,-0.3854088187,-3.5681832964
C,0,-0.0158341661,0.6297559932,-2.8154552634
C,0,0.834323189,0.3260072465,-1.7498689759
C,0,1.0548029522,-1.0216762297,-1.4468081162
C,0,0.4560611736,-2.0351484761,-2.1901896536
C,0,1.5106711579,1.4090793662,-0.9524333367
H,0,-0.8435681303,-2.5084780767,-3.8430922843
H,0,-1.2622235815,-0.1248757043,-4.4015894479
H,0,-0.1975336652,1.6682750395,-3.0757085567
H,0,1.7076604648,-1.2790260638,-0.6186017814
H,0,0.6452265881,-3.0715486264,-1.9354986007
H,0,1.1205542018,2.3946066676,-1.2070417205
H,0,2.5852809364,1.4112697377,-1.1491142059
H,0,1.3762901079,1.250933559,0.1195337951
N,0,-2.4219556076,-0.0536719241,-1.3599804112
O,0,-1.8667142432,-0.7508207122,-0.703451483
O,0,-3.055609469,0.6408881834,-1.9493333302
F,0,-5.8769339257,1.4560727858,3.8574906321
B,0,-5.9597874586,1.2753780245,2.4930012681
F,0,-7.2136219143,1.6426927191,2.0515087602
F,0,-5.0072044253,2.0530330785,1.8668705074
F,0,-5.7373760999,-0.052165543,2.188942708

Pi Complex NO2BF4 PCM ONIOM 3.248_93896
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.275067786382

Zero-point correction= 0.158745 (Hartree/Particle)

Thermal correction to Energy= 0.175238
Thermal correction to Enthalpy= 0.176182
Thermal correction to Gibbs Free Energy= 0.112467
Sum of electronic and ZPE= -476.892687
Sum of electronic and thermal Energies= -476.876194
Sum of electronic and thermal Enthalpies= -476.875250
Sum of electronic and thermal Free Energies= -476.938965

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.964 55.489 134.101

C,0,3.5249535956,-0.291063291,-0.3771040656
C,0,3.0036475868,0.6705888164,-1.2390925997
C,0,1.928923396,1.4651535649,-0.842961387
C,0,1.3494502361,1.3203605984,0.4204715227
C,0,1.8740310426,0.3445688833,1.2740381407
C,0,2.95465938,-0.4554579821,0.8817237979
C,0,0.1763112019,2.165886544,0.8370132903
H,0,4.36690136,-0.9013633945,-0.679888728
H,0,3.4365282365,0.80706279,-2.223214615
H,0,1.5353419105,2.211547304,-1.5252566836
H,0,1.4471169667,0.2177244852,2.2647490382
H,0,3.3550999553,-1.1906370116,1.5712560955
H,0,0.1042123026,2.2352022605,1.9226117232
H,0,-0.7638403567,1.7380288385,0.4673881845
H,0,0.2565856946,3.1744839512,0.4306899611
N,0,0.6448645055,-1.7695106898,-0.1114779477
O,0,0.4791952207,-2.3559668065,0.8185844365
O,0,0.7278215631,-1.2898037873,-1.1074020655
F,0,-3.8941655918,-0.8027882436,-0.4290584879
B,0,-2.8588254925,0.0512565423,-0.1174553582
F,0,-1.7374973577,-0.7006044168,0.2007285717
F,0,-2.5773058449,0.8485773679,-1.2052922515
F,0,-3.2098125109,0.8328846766,0.9609254272

Pi Complex NO2BF4 PCM ONIOM 3.254_94079
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.265925774039

Zero-point correction= 0.157622 (Hartree/Particle)
Thermal correction to Energy= 0.174936
Thermal correction to Enthalpy= 0.175881
Thermal correction to Gibbs Free Energy= 0.104925
Sum of electronic and ZPE= -476.888102
Sum of electronic and thermal Energies= -476.870787
Sum of electronic and thermal Enthalpies= -476.869843
Sum of electronic and thermal Free Energies= -476.940798

E CV S

KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.774 55.769 149.338

C,0,3.425335309,-1.722943777,0.628501027
C,0,3.4320424318,-1.301367379,-0.6978954169
C,0,3.4971661006,0.0636655271,-1.00352267
C,0,3.561505987,1.0236379051,0.0085249099
C,0,3.5460059187,0.5835382661,1.3362941534
C,0,3.4795385607,-0.771990587,1.6458627619
C,0,3.6503955642,2.4932834664,-0.3051271248
H,0,3.3808797429,-2.7790352325,0.8659213947
H,0,3.3997317836,-2.0299688209,-1.5010045214
H,0,3.5161913015,0.3795509575,-2.0423409929
H,0,3.5898606084,1.3148748894,2.1373560475
H,0,3.4707952957,-1.0871898989,2.6828631083
H,0,2.8375045568,3.0452254719,0.1719963793
H,0,3.6057147055,2.6756491674,-1.3786634052
H,0,4.5882321116,2.9083581802,0.0704779821
N,0,0.6764390983,-0.4607364284,-0.5713768408
O,0,0.5073087809,-0.7640459326,-1.6251506491
O,0,0.7489276069,-0.1491848529,0.4882048653
F,0,-3.9026291587,-0.8725008469,-0.5527363097
B,0,-4.6939316473,0.0801266036,0.0561465217
F,0,-5.3081797088,0.8504277576,-0.9089444282
F,0,-5.6489287313,-0.5422146453,0.832001942
F,0,-3.9066922179,0.885476209,0.853495266

Pi Complex NO2BF4 PCM ONIOM 3.256_93794
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267615559467

Zero-point correction= 0.158233 (Hartree/Particle)
Thermal correction to Energy= 0.175190
Thermal correction to Enthalpy= 0.176134
Thermal correction to Gibbs Free Energy= 0.109174
Sum of electronic and ZPE= -476.888887
Sum of electronic and thermal Energies= -476.871930
Sum of electronic and thermal Enthalpies= -476.870986
Sum of electronic and thermal Free Energies= -476.937945

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.933 55.587 140.929

C,0,-3.708791379,-0.3555545686,0.5158990411
C,0,-3.2939669549,0.0264731199,-0.7559680974
C,0,-2.0662136553,-0.4212478995,-1.2597075
C,0,-1.2410230952,-1.2616253645,-0.5069426738
C,0,-1.6684501771,-1.6259386684,0.7736488876
C,0,-2.8863314306,-1.1800721434,1.2812999611

C,0,0.0729195539,-1.7578270393,-1.0478219027
H,0,-4.661392756,-0.0171504063,0.9050982881
H,0,-3.9272096378,0.6583717945,-1.3693202405
H,0,-1.7615517305,-0.1308223094,-2.2607462243
H,0,-1.0403374095,-2.2727986011,1.378161719
H,0,-3.1956377745,-1.4818600778,2.2751209581
H,0,0.156301709,-1.5731040201,-2.1188705378
H,0,0.1814756898,-2.8299463287,-0.876533873
H,0,0.9184505283,-1.264114552,-0.5541394814
N,0,-1.3969890213,1.9197703666,0.2222704431
O,0,-1.4773767508,2.564008089,-0.678441976
O,0,-1.2681291724,1.373782008,1.176964389
F,0,2.4822248341,-0.1288853649,1.196700436
B,0,3.2795267076,0.0491583139,0.0844172341
F,0,4.4358347281,0.7024439293,0.4583474173
F,0,3.5998474614,-1.1738999126,-0.4660927913
F,0,2.6080857328,0.8168276353,-0.8460874763

Pi Complex NO2BF4 PCM ONIOM 3.261_94154
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.267181450224

Zero-point correction= 0.157401 (Hartree/Particle)
Thermal correction to Energy= 0.174735
Thermal correction to Enthalpy= 0.175679
Thermal correction to Gibbs Free Energy= 0.104682
Sum of electronic and ZPE= -476.888823
Sum of electronic and thermal Energies= -476.871489
Sum of electronic and thermal Enthalpies= -476.870544
Sum of electronic and thermal Free Energies= -476.941542

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.648 55.831 149.426

C,0,1.8632498918,-0.5860276355,4.873613152
C,0,0.484904449,-0.5805771256,5.0622245772
C,0,-0.144762111,-1.6642205899,5.6874849107
C,0,0.5914845912,-2.7623299104,6.1393055769
C,0,1.9747600455,-2.7558647477,5.9318945489
C,0,2.6053377437,-1.6830705119,5.3078583129
C,0,-0.0705433643,-3.9233474666,6.831510365
H,0,2.3542042082,0.2534246816,4.3964281956
H,0,-0.1066311858,0.2696429091,4.7404723569
H,0,-1.2193111478,-1.6400274148,5.8430065994
H,0,2.5647676024,-3.6029931006,6.2674750068
H,0,3.6791724501,-1.7031367012,5.1621840222
H,0,0.3432440021,-4.058591774,7.8328765772
H,0,0.0957045464,-4.855393965,6.2846119845
H,0,-1.145434657,-3.770731623,6.927345992

N,0,0.0172034908,-2.4562767681,2.9420023376
O,0,1.0196766563,-2.9108347448,3.0604039803
O,0,-0.9920195571,-2.0511763435,2.718943705
F,0,0.0098477318,-6.829550885,2.8644119663
B,0,-0.718200767,-7.6106895596,3.7387268088
F,0,-0.0920957164,-8.8286516678,3.8986942441
F,0,-0.8060096819,-6.970795258,4.9576576562
F,0,-1.9860786208,-7.8027310978,3.2300465234

Pi Complex NO2BF4 PCM ONIOM 3.270_93741
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266875078925

Zero-point correction= 0.158228 (Hartree/Particle)
Thermal correction to Energy= 0.175144
Thermal correction to Enthalpy= 0.176088
Thermal correction to Gibbs Free Energy= 0.109002
Sum of electronic and ZPE= -476.888187
Sum of electronic and thermal Energies= -476.871270
Sum of electronic and thermal Enthalpies= -476.870326
Sum of electronic and thermal Free Energies= -476.937412

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.904 55.594 141.194

C,0,1.8330917235,-0.6380460466,-4.5977882386
C,0,1.1600159759,-1.856601104,-4.5820069289
C,0,-0.1949869393,-1.908903089,-4.2588732926
C,0,-0.908126644,-0.7492258692,-3.9455392555
C,0,-0.2181380454,0.4678722053,-3.948354176
C,0,1.1403222368,0.5265284132,-4.2770675779
C,0,-2.3826179088,-0.8003639275,-3.6479843865
H,0,2.8843735903,-0.5949253592,-4.8557354846
H,0,1.6896427225,-2.7709897925,-4.8226373585
H,0,-0.7068893789,-2.8656295485,-4.252920099
H,0,-0.7519653182,1.3836273999,-3.7105582243
H,0,1.6486788215,1.4845640444,-4.2914311427
H,0,-2.6783935664,-0.0132941492,-2.9514261636
H,0,-2.6703943538,-1.7636195609,-3.2257941888
H,0,-2.9565637419,-0.6576427601,-4.5671456037
N,0,1.1111686223,-0.0636534476,-1.4603376231
O,0,1.203021374,-1.1492619782,-1.6575217171
O,0,1.0548056519,1.0027731063,-1.1578734211
F,0,-3.9459674603,1.6370161991,1.4235012149
B,0,-3.6060497899,0.500016731,0.7210415667
F,0,-3.4384563324,0.8154202095,-0.6117258241
F,0,-2.4249017525,-0.0118108924,1.2191424155
F,0,-4.6042395869,-0.4425493836,0.8508280094

Pi Complex NO2BF4 PCM ONIOM 3.276_94050
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.273363507590

Zero-point correction= 0.158064 (Hartree/Particle)
Thermal correction to Energy= 0.175049
Thermal correction to Enthalpy= 0.175993
Thermal correction to Gibbs Free Energy= 0.109095
Sum of electronic and ZPE= -476.891538
Sum of electronic and thermal Energies= -476.874553
Sum of electronic and thermal Enthalpies= -476.873609
Sum of electronic and thermal Free Energies= -476.940507

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.845 55.731 140.800

Pi Complex NO2BF4 PCM ONIOM 3.283_94088
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.265866408341

Zero-point correction= 0.157384 (Hartree/Particle)
Thermal correction to Energy= 0.174727
Thermal correction to Enthalpy= 0.175671
Thermal correction to Gibbs Free Energy= 0.104736
Sum of electronic and ZPE= -476.888238
Sum of electronic and thermal Energies= -476.870895
Sum of electronic and thermal Enthalpies= -476.869951
Sum of electronic and thermal Free Energies= -476.940886

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.643 55.832 149.296

C,0,-2.9038078398,-1.9702470564,-0.3773982697
C,0,-3.3169064663,-1.6348291921,0.9097827279
C,0,-3.7810815293,-0.3510004836,1.187637706
C,0,-3.8459789644,0.6258622926,0.1900001665
C,0,-3.4162107602,0.2825981417,-1.0952517632
C,0,-2.9521189735,-1.0059182524,-1.380524605
C,0,-4.391855161,1.9972599219,0.4857064058
H,0,-2.5468185102,-2.9694957416,-0.5961049428
H,0,-3.2749436684,-2.3737181866,1.7017837261
H,0,-4.0992465898,-0.1032588549,2.1952847049
H,0,-3.4625042021,1.0225803709,-1.8889868725
H,0,-2.6398197938,-1.2526060449,-2.3897514817
H,0,-4.1231873763,2.3234778627,1.4913771294
H,0,-5.4829596702,1.9903562278,0.4231203877
H,0,-4.0248490177,2.7354312809,-0.2282083332

N,0,-0.626197699,0.395276516,-0.3722794947
O,0,-0.8203743693,0.0596578695,0.6644734691
O,0,-0.33991566,0.7576099764,-1.3812419393
F,0,4.7689409187,0.6702141974,-1.0391548319
B,0,4.6907398998,0.0432035298,0.1872202617
F,0,3.7441199936,-0.9593397743,0.1293807516
F,0,5.9161021496,-0.4994722148,0.5109560691
F,0,4.3217042898,0.9622656139,1.1480820282

Pi Complex NO2BF4 PCM ONIOM 3.283_94208
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266064245120

Zero-point correction= 0.157474 (Hartree/Particle)
Thermal correction to Energy= 0.174973
Thermal correction to Enthalpy= 0.175917
Thermal correction to Gibbs Free Energy= 0.103642
Sum of electronic and ZPE= -476.888250
Sum of electronic and thermal Energies= -476.870751
Sum of electronic and thermal Enthalpies= -476.869807
Sum of electronic and thermal Free Energies= -476.942082

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.797 55.812 152.115

C,0,-3.2821416793,-1.9099712114,-0.0495288547
C,0,-3.2511819427,-1.1456738265,1.113328822
C,0,-3.463393069,0.2366361793,1.0522692611
C,0,-3.7154661462,0.8735379249,-0.1657556704
C,0,-3.7316640781,0.0925642537,-1.3257693752
C,0,-3.5191705835,-1.2826958671,-1.2710176684
C,0,-3.9867736581,2.3527708885,-0.2315840729
H,0,-3.1221005292,-2.9804987698,-0.0051957278
H,0,-3.0753153105,-1.6197955256,2.0730680447
H,0,-3.4517871973,0.8207275979,1.9678191384
H,0,-3.913959649,0.5691935336,-2.2837574349
H,0,-3.5371699864,-1.8656187484,-2.1846645116
H,0,-5.0550024649,2.5353661542,-0.3715765618
H,0,-3.4645065417,2.8147748285,-1.0710979256
H,0,-3.6809345593,2.855981414,0.6859481598
N,0,-0.6514952715,-0.0266776263,0.5099307724
O,0,-0.8107934822,-0.1496979432,-0.5785235322
O,0,-0.3909074041,0.1107454837,1.5798409583
F,0,3.7754863154,0.6876935651,-0.8964249574
B,0,4.7198369729,0.0476315636,-0.1200725995
F,0,5.5170377843,-0.7403443378,-0.9233234465
F,0,5.4959376166,0.986580642,0.5262157847
F,0,4.0829828636,-0.744455173,0.8132993976

Pi Complex NO2BF4 PCM ONIOM 3.289_93970
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.265951522336

Zero-point correction= 0.157904 (Hartree/Particle)
Thermal correction to Energy= 0.175175
Thermal correction to Enthalpy= 0.176120
Thermal correction to Gibbs Free Energy= 0.106005
Sum of electronic and ZPE= -476.887805
Sum of electronic and thermal Energies= -476.870534
Sum of electronic and thermal Enthalpies= -476.869590
Sum of electronic and thermal Free Energies= -476.939704

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.924 55.714 147.568

C,0,1.241798972,1.0525571351,-3.4186581415
C,0,1.3243043442,2.431982516,-3.252009379
C,0,2.5487530395,3.028774545,-2.9304489463
C,0,3.7077250032,2.2615856063,-2.7803874794
C,0,3.604460384,0.8765066587,-2.9403640808
C,0,2.3876377154,0.2768248236,-3.2564454015
C,0,5.0353740273,2.9064744945,-2.4843611596
H,0,0.2964240757,0.5875320494,-3.6711027601
H,0,0.4428476062,3.050788378,-3.3820175478
H,0,2.6046741899,4.107452576,-2.8153919031
H,0,4.4894567402,0.2605249827,-2.817175742
H,0,2.3340330942,-0.79914316,-3.375895389
H,0,5.6180862336,3.008706474,-3.4032597631
H,0,5.6224760203,2.3043331428,-1.7892508909
H,0,4.9096620552,3.9028397673,-2.0596741312
N,0,1.4999120489,2.257305761,-0.3680999651
O,0,1.9306332577,1.2384725216,-0.4178547847
O,0,1.0451048506,3.2578294776,-0.2174581243
F,0,3.1265811835,6.3908005569,4.4151143966
B,0,2.2302347926,6.0552387474,3.4223106267
F,0,2.0135320505,4.6923454087,3.4405260046
F,0,1.0362743522,6.7124955372,3.6331550999
F,0,2.7456598628,6.4198019003,2.1954836617

Pi Complex NO2BF4 PCM ONIOM 3.296_93743
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.278823983601

Zero-point correction= 0.158995 (Hartree/Particle)
Thermal correction to Energy= 0.175310
Thermal correction to Enthalpy= 0.176255
Thermal correction to Gibbs Free Energy= 0.113001
Sum of electronic and ZPE= -476.891442

Sum of electronic and thermal Energies= -476.875127
Sum of electronic and thermal Enthalpies= -476.874182
Sum of electronic and thermal Free Energies= -476.937436

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 110.009 55.298 133.128

C,0,1.8532104707,3.3914186689,-0.7992869791
C,0,1.1813012331,2.9801543081,0.3478140485
C,0,1.7632908503,2.0333559467,1.1986076572
C,0,3.027236593,1.4938907167,0.926738874
C,0,3.6800717101,1.9075692176,-0.2353400674
C,0,3.1011306402,2.8453678981,-1.0900544283
C,0,3.6691852608,0.523830436,1.8818573473
H,0,1.4084507747,4.12353082,-1.4620807223
H,0,0.2099523278,3.3958642396,0.5920857749
H,0,1.2370117252,1.7278808854,2.0985186908
H,0,4.6536261979,1.4932875918,-0.4756780646
H,0,3.6287031264,3.1492305855,-1.9867757001
H,0,4.2179982655,1.0663869859,2.6556834346
H,0,4.3757383086,-0.1302781317,1.3700819734
H,0,2.9233246322,-0.0961927068,2.3818406351
N,0,0.5357478833,0.3719741515,-0.6739207616
O,0,1.3030070977,0.4999792936,-1.4645780635
O,0,-0.3010715895,0.1422072857,0.0228914227
F,0,1.791872477,-3.5104202189,-1.9824985142
B,0,0.8714671522,-2.9030246095,-1.1623467655
F,0,0.0694403782,-2.0437902341,-1.8940398302
F,0,0.0974224306,-3.8470007958,-0.5307336101
F,0,1.5158739541,-2.1127416345,-0.2242362514

Pi Complex NO2BF4 PCM ONIOM 3.302_93903
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266382473702

Zero-point correction= 0.157948 (Hartree/Particle)
Thermal correction to Energy= 0.175123
Thermal correction to Enthalpy= 0.176067
Thermal correction to Gibbs Free Energy= 0.107173
Sum of electronic and ZPE= -476.888265
Sum of electronic and thermal Energies= -476.871090
Sum of electronic and thermal Enthalpies= -476.870146
Sum of electronic and thermal Free Energies= -476.939039

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.891 55.679 144.998

C,0,3.8961618877,-3.9854246303,0.381193286

C,0,4.6652612052,-2.8591674481,0.6620799779
C,0,4.5333371865,-2.2029490087,1.8849112502
C,0,3.6349840108,-2.6553225098,2.8538024541
C,0,2.8557445741,-3.7788624378,2.5549653955
C,0,2.9864848295,-4.4430560411,1.3312229468
C,0,3.5277984705,-1.9746412817,4.1919117626
H,0,4.0021084413,-4.4992752945,-0.5664664813
H,0,5.3704984036,-2.4874155018,-0.0720943186
H,0,5.1391198575,-1.3262829618,2.0904010423
H,0,2.153883547,-4.1525195967,3.2951667719
H,0,2.3841887246,-5.3225069998,1.1302858197
H,0,3.8241908999,-0.9270971653,4.1297536505
H,0,4.1836882514,-2.4622119776,4.9175468039
H,0,2.5105526195,-2.0215495693,4.5855545901
N,0,1.098618489,-2.2935594592,0.8491833191
O,0,1.9065918341,-1.6375205815,0.4721336778
O,0,0.2186566512,-2.8851087153,1.1768891123
F,0,0.6086899595,2.273221099,5.2328650239
B,0,0.0597724779,1.0964116549,4.7689270881
F,0,-1.161371971,0.8840078026,5.3738879535
F,0,-0.11438923,1.1784151343,3.4022244002
F,0,0.9042349802,0.0447507896,5.0588406734

Pi Complex NO2BF4 PCM ONIOM 3.319_94023
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266855800930

Zero-point correction= 0.158045 (Hartree/Particle)
Thermal correction to Energy= 0.175335
Thermal correction to Enthalpy= 0.176279
Thermal correction to Gibbs Free Energy= 0.105622
Sum of electronic and ZPE= -476.887813
Sum of electronic and thermal Energies= -476.870523
Sum of electronic and thermal Enthalpies= -476.869579
Sum of electronic and thermal Free Energies= -476.940236

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 110.024 55.679 148.710

C,0,-1.3817621703,-1.7195658655,-0.3056386346
C,0,-2.3341081933,-1.8821994355,0.6984735157
C,0,-3.4617434,-1.0656099306,0.7371504442
C,0,-3.6674302226,-0.0696101546,-0.222089783
C,0,-2.701298985,0.0915631611,-1.2196151804
C,0,-1.566832466,-0.7274216687,-1.2644352941
C,0,-4.8870316867,0.8116733591,-0.1628693936
H,0,-0.5078220948,-2.3590937164,-0.3420712656
H,0,-2.2009475001,-2.650401368,1.4514565761
H,0,-4.1991706156,-1.2079534281,1.5205850185

H,0,-2.8444270518,0.8476044562,-1.9860135404
H,0,-0.8403123935,-0.5958529921,-2.0592762385
H,0,-5.776470275,0.2291542547,0.0813963174
H,0,-5.0583855486,1.3179054626,-1.1128407326
H,0,-4.7767634371,1.5761564632,0.6108612762
N,0,-0.92077744,1.4516294727,0.5621616085
O,0,-1.2269212131,0.8457186693,1.4366758605
O,0,-0.5687060217,2.1276265574,-0.2443262001
F,0,4.668625193,-1.0729110492,0.7313269688
B,0,4.0676192874,-0.0941090705,-0.0318219594
F,0,3.5223805939,0.8642810948,0.7983080018
F,0,5.0034021024,0.4917069647,-0.8579831594
F,0,3.0656665385,-0.6564562365,-0.7961432058

Pi Complex NO2BF4 PCM ONIOM 3.330_94112
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.266691677891

Zero-point correction= 0.157728 (Hartree/Particle)
Thermal correction to Energy= 0.175120
Thermal correction to Enthalpy= 0.176064
Thermal correction to Gibbs Free Energy= 0.104458
Sum of electronic and ZPE= -476.887859
Sum of electronic and thermal Energies= -476.870467
Sum of electronic and thermal Enthalpies= -476.869523
Sum of electronic and thermal Free Energies= -476.941128

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.889 55.789 150.706

C,0,3.0320197987,-1.3799502638,-0.4393725728
C,0,2.269843893,-0.409517411,0.2077324681
C,0,1.9549205597,-0.5463353919,1.557632715
C,0,2.3944101251,-1.6502041918,2.2937011599
C,0,3.1479031603,-2.6245763297,1.6312581023
C,0,3.4690159057,-2.4911139307,0.2755538355
C,0,2.0823932058,-1.7693891545,3.7615866267
H,0,3.2798110766,-1.2733871318,-1.4887477699
H,0,1.9184100232,0.457042177,-0.3403608441
H,0,1.3611342696,0.2176072203,2.0490393038
H,0,3.5052275118,-3.4896497906,2.1825135602
H,0,4.0675944755,-3.253009243,-0.2122188512
H,0,2.1787541054,-2.798379042,4.1091264001
H,0,1.0717440826,-1.4221064961,3.9810827628
H,0,2.7730339061,-1.1561164563,4.3457725733
N,0,0.8276041006,-3.7257859213,0.4131058798
O,0,0.3434143075,-2.7451099253,0.2404387228
O,0,1.2144791052,-4.755037213,0.5634535341
F,0,1.6731385857,-6.2362816288,-2.9635981571

B,0,2.0522328216,-6.6896217868,-4.2105964289
F,0,1.682300315,-8.0110929338,-4.3479361273
F,0,1.4282319916,-5.932219741,-5.1802073123
F,0,3.4199173737,-6.573008314,-4.3462230808

Pi Complex NO2BF4 PCM ONIOM 3.366_94716
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.312820301687

Zero-point correction= 0.158348 (Hartree/Particle)
Thermal correction to Energy= 0.174303
Thermal correction to Enthalpy= 0.175247
Thermal correction to Gibbs Free Energy= 0.112432
Sum of electronic and ZPE= -476.901252
Sum of electronic and thermal Energies= -476.885297
Sum of electronic and thermal Enthalpies= -476.884353
Sum of electronic and thermal Free Energies= -476.947167

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.377 55.036 132.204

C,0,2.7691748733,-1.6212177632,-0.2947561509
C,0,1.8060982774,-1.3289340468,-1.2740571517
C,0,1.3163172761,-0.0519485052,-1.3795050563
C,0,1.7416609499,0.9579974986,-0.4579750947
C,0,2.8044544722,0.6486610873,0.4584201916
C,0,3.2920102813,-0.631887186,0.5473933723
C,0,1.344054745,2.3788346964,-0.6865888105
H,0,3.1298714946,-2.638771176,-0.1999726501
H,0,1.4519791506,-2.1114683416,-1.9317660663
H,0,0.5653517983,0.2022498349,-2.1205160129
H,0,3.1786871187,1.4374530936,1.1013973496
H,0,4.0591011889,-0.8817600473,1.2677378849
H,0,0.3156014306,2.4496515426,-1.0440244367
H,0,1.9979034433,2.7939939543,-1.4591985704
H,0,1.462750198,2.9811636608,0.2131275944
N,0,0.3814992246,0.3492199553,1.0287569629
O,0,-0.1676389057,1.3200944453,1.348075504
O,0,0.4072108143,-0.7794008259,1.2785478939
F,0,-2.3949306174,-0.4654751541,1.1301606625
B,0,-2.7432950669,-0.3071357142,-0.1972001517
F,0,-3.0331521385,-1.5300290953,-0.7580741592
F,0,-3.830651143,0.5293527983,-0.3034030676
F,0,-1.654039866,0.2550632884,-0.8414070372

Pi Complex NO2BF4 PCM ONIOM 3.372_94096
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.279061853899

Zero-point correction= 0.158195 (Hartree/Particle)
Thermal correction to Energy= 0.174932
Thermal correction to Enthalpy= 0.175876
Thermal correction to Gibbs Free Energy= 0.109974
Sum of electronic and ZPE= -476.892744
Sum of electronic and thermal Energies= -476.876007
Sum of electronic and thermal Enthalpies= -476.875062
Sum of electronic and thermal Free Energies= -476.940965

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.771 55.673 138.704

C,0,2.0012943262,3.6051234769,-0.6916612716
C,0,1.3472562672,3.2657179443,0.4867093558
C,0,1.8509047912,2.2408619644,1.2955702876
C,0,3.02254517,1.5521848426,0.9509779006
C,0,3.6624241208,1.9038027021,-0.2392528697
C,0,3.1585572511,2.9162199861,-1.0528406843
C,0,3.5813693166,0.4789177229,1.8459045569
H,0,1.614621817,4.3944621168,-1.3243088074
H,0,0.4490280045,3.7931681717,0.786674104
H,0,1.3366836434,1.9851825793,2.2176103043
H,0,4.5624063817,1.3756782853,-0.5360477888
H,0,3.671169338,3.1673862872,-1.9741150694
H,0,4.284460338,0.9097450873,2.5628751713
H,0,4.1150141851,-0.2774114156,1.2685250618
H,0,2.7923983288,-0.0182149624,2.4127671381
N,0,0.4595796396,0.6150398607,-0.4533720539
O,0,1.0792538477,0.8012786128,-1.3545957296
O,0,-0.2561111576,0.3306570111,0.3506732764
F,0,2.3522443741,-3.0663726001,-1.4008119397
B,0,1.3768188788,-2.5759548869,-0.565979282
F,0,0.3652833956,-1.9874003944,-1.3059584969
F,0,0.8671077946,-3.5825492718,0.2185541436
F,0,1.8955179476,-1.5681701204,0.2309896931

Pi Complex NO2BF4 PCM ONIOM 3.382_93727
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.277518938346

Zero-point correction= 0.158344 (Hartree/Particle)
Thermal correction to Energy= 0.174923
Thermal correction to Enthalpy= 0.175867
Thermal correction to Gibbs Free Energy= 0.112043
Sum of electronic and ZPE= -476.890975
Sum of electronic and thermal Energies= -476.874395
Sum of electronic and thermal Enthalpies= -476.873451
Sum of electronic and thermal Free Energies= -476.937275

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.766 55.659 134.329

C,0,-0.2639671368,0.1643744557,4.0367281044
C,0,-0.5501259024,1.3975450241,3.4532858604
C,0,-1.7926605863,1.6337005991,2.867780177
C,0,-2.7764878553,0.6450590339,2.8479260839
C,0,-2.4724948299,-0.5969441708,3.4260909304
C,0,-1.230648237,-0.834973727,4.0241571299
C,0,-4.1338321917,0.9065494255,2.2531728333
H,0,0.7047745643,-0.0172739407,4.4852450029
H,0,0.2000426923,2.1795398012,3.4501145739
H,0,-1.9982499821,2.5990242327,2.4181106741
H,0,-3.2183043003,-1.3869376446,3.4166047231
H,0,-1.0174362672,-1.8129016453,4.4479218484
H,0,-4.8123894041,1.2882436715,3.0201460048
H,0,-4.5759291449,-0.0055413079,1.8495440043
H,0,-4.0813071619,1.6501604273,1.4576213456
N,0,-1.1861916478,-1.2707077063,1.115413452
O,0,-1.8542907265,-2.1491138702,0.9754786489
O,0,-0.4414406185,-0.4448930381,1.084088348
F,0,-1.4043597647,-3.7128504674,2.3680745427
B,0,-0.0909041651,-3.9858976105,2.7119132267
F,0,0.6461639126,-2.8826310406,2.3107331415
F,0,0.0209678461,-4.1652921815,4.0704462019
F,0,0.3461964072,-5.1068185201,2.0468857419

Pi Complex NO2BF4 PCM ONIOM 3.406_94020
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.274295003518

Zero-point correction= 0.158065 (Hartree/Particle)
Thermal correction to Energy= 0.174880
Thermal correction to Enthalpy= 0.175825
Thermal correction to Gibbs Free Energy= 0.110851
Sum of electronic and ZPE= -476.892992
Sum of electronic and thermal Energies= -476.876178
Sum of electronic and thermal Enthalpies= -476.875233
Sum of electronic and thermal Free Energies= -476.940207

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.739 55.685 136.748

C,0,-0.0639081568,-0.3717528674,4.1883481227
C,0,-0.3037664744,1.0006098362,4.184852028
C,0,-1.6065449489,1.4896780422,4.1048562205
C,0,-2.6962164036,0.6217102659,4.0271675409
C,0,-2.4416068401,-0.757923892,4.0220238385

C,0,-1.1379186626,-1.2528723946,4.1092167154
C,0,-4.110026867,1.1372262221,3.9811334958
H,0,0.9482545207,-0.7566338113,4.2361953096
H,0,0.5266595824,1.694407915,4.241326558
H,0,-1.7772020693,2.5608249502,4.1025870503
H,0,-3.275488458,-1.451430848,3.9642806314
H,0,-0.9589590942,-2.3252232923,4.0865454615
H,0,-4.1501081792,2.160159743,3.6070669374
H,0,-4.5444894632,1.1316732306,4.9838960841
H,0,-4.7416487192,0.5103692773,3.3491901329
N,0,-1.8805018184,-0.5465102219,1.3116422001
O,0,-2.6961593657,-1.2675079796,1.0835741979
O,0,-1.0549591356,0.1898239824,1.3825598799
F,0,-0.4486284372,-4.4773773182,2.6476138121
B,0,0.4605657683,-3.6421499276,2.0359569371
F,0,-0.2158234828,-2.5692045068,1.4732271243
F,0,1.3702195088,-3.1783061667,2.9601531691
F,0,1.1221608959,-4.3235910385,1.0380945522

Pi Complex NO2BF4 PCM ONIOM 3.408_94164
ONIOM(M062X/6-311G*:PM3)
E(RPM3) = 0.274141138819

Zero-point correction= 0.158015 (Hartree/Particle)
Thermal correction to Energy= 0.174876
Thermal correction to Enthalpy= 0.175820
Thermal correction to Gibbs Free Energy= 0.109504
Sum of electronic and ZPE= -476.893138
Sum of electronic and thermal Energies= -476.876278
Sum of electronic and thermal Enthalpies= -476.875334
Sum of electronic and thermal Free Energies= -476.941649

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.736 55.710 139.573

C,0,-3.6336609423,-0.5981605817,0.5382173212
C,0,-2.9948052888,0.2803794646,1.4144871802
C,0,-2.0051518573,1.1426989958,0.9528353776
C,0,-1.6257692182,1.1474469828,-0.3929508567
C,0,-2.267218245,0.2542169655,-1.2603047855
C,0,-3.2695297758,-0.6084304646,-0.8022628686
C,0,-0.5554907934,2.0847710775,-0.885340145
H,0,-4.4079169507,-1.2632388852,0.9006527977
H,0,-3.2714849601,0.2947833477,2.4623637999
H,0,-1.5188680623,1.8231693097,1.6443756958
H,0,-1.9967461849,0.2482169451,-2.3121694495
H,0,-3.7631656604,-1.2754601803,-1.4995291138
H,0,-0.7989066481,3.1167644437,-0.6261353718

H,0,-0.4394750467,2.0234160213,-1.9673795207
H,0,0.4131700808,1.8567766628,-0.4252237879
N,0,-0.5306611919,-1.7136202805,-0.3244116655
O,0,-0.8185220633,-1.6613021067,0.7444676556
O,0,-0.1591332508,-1.8738084493,-1.3598672007
F,0,2.9391015672,1.1082499409,-0.9111009083
B,0,2.7148643009,0.5163340587,0.3124469876
F,0,3.8358738271,-0.1842404683,0.701257536
F,0,2.4213203192,1.4763828027,1.2556981268
F,0,1.6502690448,-0.3663676022,0.2068671956

TSs for Toluene + $NO_2^+BF_4^-$ M062X/6-311G*/PCM(CH_2Cl_2)
TS NO2BF4 PCM PURE-M06-2X 3.440_824095 (**5a**‡)
M062X/6-311G*
E(RM062X) = -900.938230756

Zero-point correction= 0.157181 (Hartree/Particle)
Thermal correction to Energy= 0.172152
Thermal correction to Enthalpy= 0.173096
Thermal correction to Gibbs Free Energy= 0.114136
Sum of electronic and ZPE= -900.781049
Sum of electronic and thermal Energies= -900.766079
Sum of electronic and thermal Enthalpies= -900.765135
Sum of electronic and thermal Free Energies= -900.824095

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.027 53.140 124.092

C,0,-1.0102818907,-0.433536969,1.5651973451
C,0,-0.7782877839,0.8806702567,1.1365812781
C,0,-1.6818068026,1.5052314582,0.2977331748
C,0,-2.8341488766,0.8203091025,-0.1421470076
C,0,-3.0710923804,-0.4890607882,0.3323471484
C,0,-2.1618388761,-1.1104113392,1.1745525989
C,0,-3.8539580601,1.488495173,-1.0129993114
H,0,-0.2872403082,-0.92140422,2.2085329235
H,0,0.1153129439,1.4025694958,1.4574440826
H,0,-1.5064471399,2.5210167525,-0.0405292082
H,0,-3.964883125,-1.0118360067,0.0161749292
H,0,-2.3448882918,-2.1267291697,1.5008345004
H,0,-4.6366898694,1.9247485951,-0.3857815624
H,0,-4.3325036448,0.7620326743,-1.6723652637
H,0,-3.4170700658,2.292561324,-1.6068667788
N,0,-1.4944211238,-0.3484565674,-1.8393753424
O,0,-2.1472515278,-0.0697142997,-2.7167547178
O,0,-0.5794208854,-0.7519383026,-1.3213861869
F,0,-2.3512906532,-2.5956563131,-1.796043987
B,0,-3.7574582321,-2.7949257163,-1.8912966265
F,0,-4.0290752092,-3.748807415,-2.8598446355

F,0,-4.2387787784,-3.1938519143,-0.6408984897
F,0,-4.3371304187,-1.557330811,-2.2454068632

TS NO2BF4 PCM PURE-M06-2X 3.4399_824088
M062X/6-311G*
E(RM062X) = -900.938230779

Zero-point correction= 0.157184 (Hartree/Particle)
Thermal correction to Energy= 0.172153
Thermal correction to Enthalpy= 0.173097
Thermal correction to Gibbs Free Energy= 0.114142
Sum of electronic and ZPE= -900.781047
Sum of electronic and thermal Energies= -900.766078
Sum of electronic and thermal Enthalpies= -900.765133
Sum of electronic and thermal Free Energies= -900.824088

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.028 53.139 124.081

C,0,1.6436415556,2.4802636962,0.1935466235
C,0,2.7282275088,1.7903389991,0.7524260453
C,0,2.9650375674,0.4738760967,0.4046573877
C,0,2.110240449,-0.1863268976,-0.5030579634
C,0,1.0462904869,0.5372725688,-1.0862654784
C,0,0.8139498259,1.858040236,-0.7345132671
C,0,2.3703064536,-1.597518424,-0.9340756463
H,0,1.455283704,3.506796534,0.4858400471
H,0,3.3752681769,2.2888346295,1.4642512718
H,0,3.8006407476,-0.0669250365,0.8362749187
H,0,0.4000948922,0.0428305864,-1.8004635673
H,0,-0.0268533076,2.3856281719,-1.1675987187
H,0,1.4328019345,-2.1125798751,-1.1516054772
H,0,2.9307207363,-2.1552853398,-0.182476137
H,0,2.9608816989,-1.5926658398,-1.8547180814
N,0,0.4825632177,-0.5628494073,1.2999878352
O,0,0.3958489308,-1.6778924841,1.1489206061
O,0,0.338127619,0.4209291673,1.8287933271
F,0,-0.9353662985,-1.7977018116,-1.184405516
B,0,-1.9334756999,-0.8201090709,-0.9816106465
F,0,-1.6415838612,-0.1606178413,0.2455751511
F,0,-1.8836854942,0.1180311927,-2.0168461652
F,0,-3.1829008438,-1.4158478509,-0.9055715491

TS NO2BF4 PCM PURE-M06-2X 3.440_824085
M062X/6-311G*
E(RM062X) = -900.938230783

Zero-point correction= 0.157185 (Hartree/Particle)
Thermal correction to Energy= 0.172154

Thermal correction to Enthalpy= 0.173098
Thermal correction to Gibbs Free Energy= 0.114145
Sum of electronic and ZPE= -900.781046
Sum of electronic and thermal Energies= -900.766077
Sum of electronic and thermal Enthalpies= -900.765133
Sum of electronic and thermal Free Energies= -900.824085

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.028 53.138 124.076

C,0,-0.886597005,-0.043161829,1.8571414905
C,0,-2.0661945678,0.6723635012,1.6743680607
C,0,-2.9816788786,0.254823141,0.7205945751
C,0,-2.7232839065,-0.8833805633,-0.0752940723
C,0,-1.5413154489,-1.6191159952,0.1530230016
C,0,-0.6317341918,-1.1978169148,1.1044802585
C,0,-3.7488055818,-1.342457657,-1.0664661522
H,0,-0.1591634294,0.2894978848,2.5884837855
H,0,-2.2671288229,1.5664788112,2.2514757435
H,0,-3.8975348793,0.8109551735,0.5655383636
H,0,-1.3484450811,-2.5099370653,-0.4353904184
H,0,0.2840287906,-1.754315771,1.2642985691
H,0,-4.2644392056,-0.4888149647,-1.5102528017
H,0,-4.5020931214,-1.9483949402,-0.5548194153
H,0,-3.3074530635,-1.9554938287,-1.8535253822
N,0,-1.4629604534,0.720258505,-1.4470491092
O,0,-2.1324296737,0.6514571719,-2.3530016349
O,0,-0.5448487153,1.0091167131,-0.8622748771
F,0,-4.24711686,3.0781891108,0.4898908148
B,0,-3.7905836801,3.0246898613,-0.8303473068
F,0,-4.1143386269,4.1832464573,-1.5193174679
F,0,-2.3775193478,2.8539210349,-0.8173633395
F,0,-4.3469492497,1.8987521634,-1.4751466854

TS NO2BF4 PCM PURE-M06-2X 3.426_824053 (**5b**‡)
M062X/6-311G*
E(RM062X) = -900.937046606

Zero-point correction= 0.156855 (Hartree/Particle)
Thermal correction to Energy= 0.171835
Thermal correction to Enthalpy= 0.172779
Thermal correction to Gibbs Free Energy= 0.112994
Sum of electronic and ZPE= -900.780191
Sum of electronic and thermal Energies= -900.765212
Sum of electronic and thermal Enthalpies= -900.764268
Sum of electronic and thermal Free Energies= -900.824053

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K

Total 107.828 53.127 125.828

C,0,-1.9062710451,-0.7144224971,1.1120366187
C,0,-1.4232682291,0.5169540071,1.52227902
C,0,-1.8554215488,1.6676117661,0.8685863008
C,0,-2.798263357,1.5985031769,-0.1906301725
C,0,-3.317117116,0.3361666821,-0.5466853148
C,0,-2.8624852669,-0.8008384879,0.0817617901
C,0,-3.3068079677,2.8420646507,-0.8521038305
H,0,-1.5533116659,-1.6211596146,1.5891379605
H,0,-0.6982577476,0.5878573657,2.3232499033
H,0,-1.4789733169,2.6402157078,1.1699074626
H,0,-4.0413927923,0.2744634209,-1.3492436796
H,0,-3.2367479526,-1.77233015,-0.2176784293
H,0,-4.3447250949,3.0146198741,-0.5556321238
H,0,-3.2827787038,2.7305108338,-1.9381742914
H,0,-2.7260589476,3.7191998347,-0.5660376328
N,0,-0.7227522512,1.3877473445,-1.3202750352
O,0,-0.4130523872,0.2990091677,-1.2985397925
O,0,-0.5988316137,2.457359757,-1.6826715848
F,0,-2.3724434449,0.931995471,-3.1737352246
B,0,-1.5607825096,1.4226308112,-4.2383060676
F,0,-1.9485753162,0.8423676245,-5.4343836271
F,0,-1.6919252436,2.8122899356,-4.2786498517
F,0,-0.2290434814,1.0833933185,-3.9229043976

TS NO2BF4 PCM PURE-M06-2X 3.393_822143utf00006
M062X/6-311G*
E(RM062X) = -900.935093295

Zero-point correction= 0.156998 (Hartree/Particle)
Thermal correction to Energy= 0.172023
Thermal correction to Enthalpy= 0.172967
Thermal correction to Gibbs Free Energy= 0.112950
Sum of electronic and ZPE= -900.778096
Sum of electronic and thermal Energies= -900.763070
Sum of electronic and thermal Enthalpies= -900.762126
Sum of electronic and thermal Free Energies= -900.822143

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 107.946 53.120 126.317

C,0,2.8575343716,-1.7485595972,0.7241916858
C,0,3.3218246122,-1.4760057777,-0.5447468765
C,0,3.2791891546,-0.1608185115,-1.0179554817
C,0,2.8388846154,0.904336765,-0.1877248236
C,0,2.3963782401,0.6014844355,1.1129351149
C,0,2.3897215431,-0.7047494886,1.5519409344
C,0,2.924309588,2.318423966,-0.6684298844

H,0,2.8432657198,-2.7668533343,1.0931284991
H,0,3.6585592541,-2.2675310726,-1.2003055877
H,0,3.6186307716,0.0603026368,-2.0237488332
H,0,2.0521632158,1.4017793158,1.7577645676
H,0,2.0253796567,-0.9379581822,2.545300314
H,0,2.8539392305,2.3814190427,-1.755452451
H,0,3.8995668021,2.7279821365,-0.3885490993
H,0,2.1561006551,2.946140537,-0.2167430951
N,0,0.9597482053,0.0425795253,-1.4443803582
O,0,0.4842564297,-0.7823151688,-0.8284193645
O,0,0.8894143082,0.8334285422,-2.2605548549
F,0,0.9136057951,-1.6903983293,-5.1846056559
B,0,0.748706945,-2.0006141771,-3.8398436712
F,0,0.588355936,-3.3693316097,-3.6558914209
F,0,1.8924113816,-1.5601281408,-3.1103304159
F,0,-0.3632544316,-1.3074895128,-3.3151692419

TS NO2BF4 PCM PURE-M06-2X 3.3794_822005
M062X/6-311G*
E(RM062X) = -900.935104619

Zero-point correction= 0.156812 (Hartree/Particle)
Thermal correction to Energy= 0.171848
Thermal correction to Enthalpy= 0.172792
Thermal correction to Gibbs Free Energy= 0.113099
Sum of electronic and ZPE= -900.778293
Sum of electronic and thermal Energies= -900.763257
Sum of electronic and thermal Enthalpies= -900.762312
Sum of electronic and thermal Free Energies= -900.822005

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 107.836 53.122 125.634

C,0,-2.3422577904,-2.1331702237,-0.1259724234
C,0,-1.85809662,-1.3353608632,0.888277449
C,0,-2.1088896475,0.0400310022,0.851378149
C,0,-2.9172063585,0.6126353896,-0.1669693145
C,0,-3.4227312073,-0.2296256623,-1.1733217192
C,0,-3.1235111395,-1.5748063816,-1.1606880185
C,0,-3.2784628107,2.0630660985,-0.1144563867
H,0,-2.121672389,-3.1937510893,-0.1388779352
H,0,-1.2357084737,-1.7420662726,1.6737577399
H,0,-1.7118147907,0.6806951533,1.631075373
H,0,-4.0375609866,0.1908728298,-1.9607298583
H,0,-3.4938133356,-2.2170531483,-1.9509822224
H,0,-4.2045976947,2.1752248897,0.4574726187
H,0,-3.4482216398,2.4740130645,-1.1097301083
H,0,-2.5162362047,2.6519480737,0.3982266704
N,0,-0.5976887707,0.6715984436,-0.8403477347

O,0,-0.3784371872,-0.287918325,-1.4043402596
O,0,-0.3491699985,1.758825415,-0.6080311467
F,0,2.0351003561,0.5521943624,-0.6490158623
B,0,2.0994676049,0.1950184418,0.7154208292
F,0,2.8369120484,-0.9729072702,0.8697855832
F,0,2.6484122608,1.2379014613,1.45332161
F,0,0.7599647747,-0.0322723892,1.1487359673

TS NO2BF4 PCM PURE-M06-2X 3.332_821966
M062X/6-311G*
E(RM062X) = -900.937163256

Zero-point correction= 0.157453 (Hartree/Particle)
Thermal correction to Energy= 0.171946
Thermal correction to Enthalpy= 0.172890
Thermal correction to Gibbs Free Energy= 0.115197
Sum of electronic and ZPE= -900.779710
Sum of electronic and thermal Energies= -900.765217
Sum of electronic and thermal Enthalpies= -900.764273
Sum of electronic and thermal Free Energies= -900.821966

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 107.898 52.379 121.425

C,0,-1.4950406867,-0.727259127,1.1248757157
C,0,-0.9671302018,0.572752383,1.2172511866
C,0,-1.6081955331,1.6039176077,0.5822989224
C,0,-2.7853721567,1.3541190998,-0.2040636468
C,0,-3.3504873719,0.0359741035,-0.1846857477
C,0,-2.6928247006,-0.9892434794,0.4511634979
C,0,-3.5941568161,2.5060104787,-0.7089073374
H,0,-0.968658486,-1.5442018371,1.6058266547
H,0,-0.0603532241,0.7493855787,1.781031956
H,0,-1.2256091862,2.6174646978,0.6324533296
H,0,-4.2839448157,-0.1387012772,-0.7038065206
H,0,-3.0955572352,-1.9934791686,0.425148213
H,0,-3.4530840773,3.3778242165,-0.0698479093
H,0,-4.6489843513,2.2442033471,-0.7550642797
H,0,-3.2953609895,2.7796189468,-1.7250269671
N,0,-1.5366741338,0.7915860311,-1.8403917451
O,0,-1.7922201354,1.5338145416,-2.6901490183
O,0,-0.8198723911,-0.0861743042,-1.614779772
F,0,-2.928099566,-1.0263220374,-2.9557254888
B,0,-4.2775585221,-0.6714927457,-3.1809131284
F,0,-4.6196233506,-0.8937230798,-4.5071914482
F,0,-5.092056258,-1.427411151,-2.3230674715
F,0,-4.4249788109,0.6955911751,-2.8580999948

TS NO2BF4 PCM PURE-M06-2X 2.434_821714
M062X/6-311G*
E(RM062X) = -900.935240397

Zero-point correction= 0.156994 (Hartree/Particle)
Thermal correction to Energy= 0.172169
Thermal correction to Enthalpy= 0.173113
Thermal correction to Gibbs Free Energy= 0.113527
Sum of electronic and ZPE= -900.778246
Sum of electronic and thermal Energies= -900.763071
Sum of electronic and thermal Enthalpies= -900.762127
Sum of electronic and thermal Free Energies= -900.821714

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.038 53.282 125.411

C,0,-1.8408225491,-0.9887977627,-1.3499579918
C,0,-3.0567204418,-0.6751782168,-0.7096182153
C,0,-3.2081443809,0.5356870502,-0.0378295163
C,0,-2.152792657,1.4399326882,0.0191445533
C,0,-0.9493675976,1.1275601981,-0.6534280104
C,0,-0.7970677526,-0.0540800742,-1.3470986958
C,0,-2.2648920073,2.7285068827,0.7795339174
H,0,-1.7236515385,-1.9277804049,-1.8781925737
H,0,-3.8771246502,-1.3840148148,-0.7444895564
H,0,-4.1449464914,0.7647631418,0.4574654164
H,0,-0.1321712115,1.8408556728,-0.6161112637
H,0,0.1291968336,-0.2986238572,-1.8492746053
H,0,-1.9719893802,3.5731511913,0.1523016122
H,0,-1.5930478527,2.7189293163,1.6420596407
H,0,-3.2799337084,2.8961788443,1.1378896804
N,0,-1.5033646493,-1.9118188212,0.8773709664
O,0,-1.0194529417,-1.0559878985,1.4292821061
O,0,-1.883371738,-2.966370601,0.7470355636
F,0,0.5913352275,-2.4809993953,-0.1505599389
B,0,0.5916921653,-3.2745218553,-1.3350244455
F,0,-0.6602844372,-3.9088289109,-1.4266415561
F,0,0.7621312013,-2.429029113,-2.4370186522
F,0,1.6111775577,-4.2113582596,-1.2634144351

TS NO2BF4 PCM PURE-M06-2X 2.429_821508
M062X/6-311G*
E(RM062X) = -900.935305625

Zero-point correction= 0.157249 (Hartree/Particle)
Thermal correction to Energy= 0.172359
Thermal correction to Enthalpy= 0.173303
Thermal correction to Gibbs Free Energy= 0.113798

Sum of electronic and ZPE= -900.778057
Sum of electronic and thermal Energies= -900.762947
Sum of electronic and thermal Enthalpies= -900.762003
Sum of electronic and thermal Free Energies= -900.821508

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.157 53.083 125.238

C,0,-0.8873318714,0.2541988098,1.4844612488
C,0,-2.1530203705,0.8564791654,1.365946353
C,0,-3.1303394847,0.2617036118,0.5836453864
C,0,-2.8743127181,-0.9468594736,-0.0738040271
C,0,-1.6246308826,-1.56893604,0.1013743991
C,0,-0.6428739491,-0.9901715261,0.880035979
C,0,-3.9066624156,-1.583250754,-0.9572950203
H,0,-0.1136717436,0.7110006717,2.088710938
H,0,-2.3522665534,1.7935483055,1.8736984626
H,0,-4.0983339284,0.7369757723,0.4708170955
H,0,-1.4318380602,-2.5135298397,-0.3964210153
H,0,0.3232189603,-1.4640983507,0.9976789371
H,0,-3.5704577513,-1.5747936865,-1.9976570743
H,0,-4.8616969003,-1.0620820213,-0.9014544158
H,0,-4.0610634357,-2.6276443174,-0.6778283815
N,0,-0.3203710188,1.4620740833,-0.5448390208
O,0,-0.9246565988,0.9620998225,-1.3506008588
O,0,0.3826384836,2.2150595526,-0.0887592391
F,0,2.0522095282,0.433221183,1.0967544864
B,0,2.4528895355,-0.2825675004,-0.0484706186
F,0,3.7052147943,0.1402358728,-0.4687324671
F,0,2.4509760441,-1.6513067589,0.2279047263
F,0,1.4938413368,-0.0199225823,-1.0700888734

TS NO2BF4 PCM PURE-M06-2X 2.4410_821447
M062X/6-311G*
E(RM062X) = -900.935135332

Zero-point correction= 0.157115 (Hartree/Particle)
Thermal correction to Energy= 0.172245
Thermal correction to Enthalpy= 0.173190
Thermal correction to Gibbs Free Energy= 0.113688
Sum of electronic and ZPE= -900.778020
Sum of electronic and thermal Energies= -900.762890
Sum of electronic and thermal Enthalpies= -900.761946
Sum of electronic and thermal Free Energies= -900.821447

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.086 53.174 125.231

C,0,-1.7762903842,-0.9983838729,-1.3188325103
C,0,-2.9843544479,-0.7333762897,-0.6604744483
C,0,-3.137258466,0.4627602415,0.00895485
C,0,-2.1189005656,1.4445969125,0.0050206814
C,0,-0.9459894557,1.1970632204,-0.6972636303
C,0,-0.7629131335,-0.018775074,-1.3500185638
C,0,-2.3172715464,2.7185586937,0.772199702
H,0,-1.6364277729,-1.933209418,-1.8500746449
H,0,-3.7753191734,-1.4733293986,-0.6563174208
H,0,-4.0560593785,0.6657181391,0.5498785937
H,0,-0.1437396469,1.9242913123,-0.7096618127
H,0,0.1664966491,-0.217905124,-1.8695800682
H,0,-1.5726544537,3.4665100615,0.5028267823
H,0,-2.2334941323,2.5273185467,1.8458123514
H,0,-3.3122201995,3.1307904893,0.5932077418
N,0,-0.4128900122,-1.5244689998,0.6363324694
O,0,-0.8711369301,-0.8967509837,1.4531185155
O,0,0.2201466732,-2.3605623113,0.2165849809
F,0,1.5051509282,-0.0378859489,0.7193339903
B,0,2.3889852687,0.0387357624,-0.3945759835
F,0,2.1804452874,-1.1068443857,-1.1835599416
F,0,2.0699890293,1.1798857906,-1.1415751985
F,0,3.6998758631,0.0929296367,0.0548295641

TS NO2BF4 PCM PURE-M06-2X 2.419_821322utf00003
M062X/6-311G*
E(RM062X) = -900.935062628

Zero-point correction= 0.157106 (Hartree/Particle)
Thermal correction to Energy= 0.172184
Thermal correction to Enthalpy= 0.173129
Thermal correction to Gibbs Free Energy= 0.113741
Sum of electronic and ZPE= -900.777956
Sum of electronic and thermal Energies= -900.762878
Sum of electronic and thermal Enthalpies= -900.761934
Sum of electronic and thermal Free Energies= -900.821322

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.047 53.192 124.992

C,0,-3.2703514393,-1.043692062,-0.6890301725
C,0,-3.7744870497,-0.0953723686,0.2170112521
C,0,-3.0294739291,1.0329354822,0.50438874
C,0,-1.7961856488,1.2597091742,-0.1315669504
C,0,-1.3485554388,0.3549041005,-1.1025628414
C,0,-2.0698285975,-0.7886997483,-1.3831414592
C,0,-0.9377160985,2.4342214352,0.2282116027
H,0,-3.8462216353,-1.9335468756,-0.9163860085
H,0,-4.7238368527,-0.2694888268,0.7092163049

H,0,-3.388365271,1.7469785659,1.2374283651
H,0,-0.3987128096,0.520685945,-1.5932793261
H,0,-1.6880959314,-1.5070122317,-2.097857078
H,0,0.0174675708,2.0762430912,0.6217991818
H,0,-1.4086401218,3.0725831335,0.9746209194
H,0,-0.7151774509,3.0339754055,-0.6572048653
N,0,-1.8565960702,-2.0343158678,1.0052375321
O,0,-1.3001461621,-1.1743510303,1.4676271687
O,0,-2.1991260017,-3.1067197303,0.8968146061
F,0,0.9638204634,-1.3430042337,-1.9571330906
B,0,1.1313498872,-1.7400263707,-0.6249948872
F,0,2.3499781708,-2.3856165868,-0.4558202221
F,0,1.0450175464,-0.6252891133,0.2242659698
F,0,0.0752068698,-2.6359922872,-0.2854377414

TS NO2BF4 PCM PURE-M06-2X 2.4198_821288
M062X/6-311G*
E(RM062X) = -900.935162090

Zero-point correction= 0.157359 (Hartree/Particle)
Thermal correction to Energy= 0.172449
Thermal correction to Enthalpy= 0.173393
Thermal correction to Gibbs Free Energy= 0.113874
Sum of electronic and ZPE= -900.777803
Sum of electronic and thermal Energies= -900.762713
Sum of electronic and thermal Enthalpies= -900.761769
Sum of electronic and thermal Free Energies= -900.821288

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.213 53.101 125.269

C,0,1.958519396,-1.1145535613,1.2372194673
C,0,2.9921891799,-0.6647537294,0.4016029895
C,0,2.8946141314,0.5825503364,-0.1856624473
C,0,1.7987172951,1.4230672573,0.0833960692
C,0,0.824386326,1.0058223841,0.9963938127
C,0,0.8898892691,-0.2524525927,1.5639623904
C,0,1.6395379029,2.7402345363,-0.6124038477
H,0,2.0201555375,-2.0946302162,1.6966360233
H,0,3.8386604885,-1.30801219,0.1929755168
H,0,3.6638694311,0.9194970828,-0.8721185679
H,0,-0.0235497833,1.6442606884,1.2068744202
H,0,0.1054252939,-0.5896311565,2.2312269769
H,0,1.4928520284,3.544545296,0.1117369549
H,0,0.7446248618,2.7055204344,-1.2394704405
H,0,2.4998131209,2.9803944518,-1.236033176
N,0,0.5253886261,-1.7255958592,-0.6143746453
O,0,0.6004230604,-0.8647132023,-1.3328494699
O,0,0.229541878,-2.7601741867,-0.2657868239

F,0,-2.1823492115,0.9269081215,1.1523506517
B,0,-2.1730384262,0.3227602284,-0.1097543069
F,0,-1.3141148409,1.0231871414,-0.9738314387
F,0,-1.6725968696,-1.0047150415,0.0293992539
F,0,-3.4563056955,0.2743207769,-0.6401113627

TS NO2BF4 PCM PURE-M06-2X 2.435_821006
M062X/6-311G*
E(RM062X) = -900.935138423

Zero-point correction= 0.157267 (Hartree/Particle)
Thermal correction to Energy= 0.172246
Thermal correction to Enthalpy= 0.173191
Thermal correction to Gibbs Free Energy= 0.114132
Sum of electronic and ZPE= -900.777872
Sum of electronic and thermal Energies= -900.762892
Sum of electronic and thermal Enthalpies= -900.761948
Sum of electronic and thermal Free Energies= -900.821006

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.086 53.055 124.299

C,0,-2.7315304569,-1.0596366729,-0.8525009019
C,0,-3.458684925,-0.3572834215,0.1162700198
C,0,-3.016662594,0.8866925373,0.5197973687
C,0,-1.8754072091,1.4854905471,-0.0605531748
C,0,-1.212115834,0.8204648143,-1.0868576522
C,0,-1.6196849842,-0.449126754,-1.4725050947
C,0,-1.3645565641,2.7934783096,0.4598825832
H,0,-3.0542441951,-2.0437336525,-1.1735439675
H,0,-4.3359196318,-0.8047193023,0.5672673939
H,0,-3.5457698826,1.4182167488,1.3041652072
H,0,-0.332214603,1.2624223012,-1.5373011525
H,0,-1.0714897918,-0.9844238398,-2.2391170118
H,0,-0.7973120468,2.6153313112,1.37731235
H,0,-2.1824266924,3.4780109491,0.690906031
H,0,-0.6881246206,3.2641241999,-0.2528650322
N,0,-0.8679100538,-1.7183252024,0.5697389992
O,0,-0.804362628,-0.8864405169,1.3251418752
O,0,-0.6467529113,-2.7508054224,0.1582715094
F,0,1.9225738371,1.04422706,-1.2954986763
B,0,1.8389976723,0.2686769285,-0.1355620336
F,0,3.1053135788,-0.005367248,0.3672307874
F,0,1.0648088569,0.9356669404,0.8290947868
F,0,1.1880076794,-0.9607566147,-0.4516142143

TS NO2BF4 PCM PURE-M06-2X 2.424_820983
M062X/6-311G*
E(RM062X) = -900.933886364

Zero-point correction= 0.157049 (Hartree/Particle)
Thermal correction to Energy= 0.172252
Thermal correction to Enthalpy= 0.173196
Thermal correction to Gibbs Free Energy= 0.112903
Sum of electronic and ZPE= -900.776837
Sum of electronic and thermal Energies= -900.761635
Sum of electronic and thermal Enthalpies= -900.760690
Sum of electronic and thermal Free Energies= -900.820983

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.090 53.155 126.897

C,0,-0.9802296939,0.283338448,1.464761148
C,0,-2.2960323043,0.7185035574,1.2200391317
C,0,-3.1550753693,-0.0696781611,0.4715792865
C,0,-2.7306701865,-1.3074341556,-0.0255699919
C,0,-1.4341839381,-1.7604565433,0.2807218202
C,0,-0.5691757213,-0.9866099429,1.0270880331
C,0,-3.6313016069,-2.144954244,-0.8845116379
H,0,-0.295921351,0.8902559124,2.0442825747
H,0,-2.625182796,1.67795811,1.603002526
H,0,-4.1613537639,0.2740173228,0.2592304292
H,0,-1.1129605238,-2.728525157,-0.0892021388
H,0,0.4352336558,-1.3226643962,1.2465676715
H,0,-3.2920906247,-2.1134875857,-1.9239516183
H,0,-4.6610620194,-1.7904802912,-0.8534619006
H,0,-3.6086380745,-3.1896906027,-0.5694427316
N,0,-0.4260726418,1.3001655673,-0.6651370444
O,0,0.1723767563,2.1715534037,-0.2737807017
O,0,-0.9300651005,0.6505688427,-1.4324375966
F,0,1.9678413544,0.6538921797,1.2726276169
B,0,2.551506657,0.4819647048,0.0020953954
F,0,3.617367127,-0.4007625802,0.0713442553
F,0,1.5455853972,-0.0498487123,-0.8600311503
F,0,2.944163768,1.7222123232,-0.5005053766

TS NO2BF4 PCM PURE-M06-2X 2.398_820850
M062X/6-311G*
E(RM062X) = -900.934626828

Zero-point correction= 0.157042 (Hartree/Particle)
Thermal correction to Energy= 0.172053
Thermal correction to Enthalpy= 0.172997
Thermal correction to Gibbs Free Energy= 0.113776
Sum of electronic and ZPE= -900.777585
Sum of electronic and thermal Energies= -900.762574
Sum of electronic and thermal Enthalpies= -900.761630
Sum of electronic and thermal Free Energies= -900.820850

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 107.965 53.086 124.640

C,0,2.7322567431,-0.995166805,0.5470515269
C,0,3.3246728059,-0.2463328388,-0.4748262467
C,0,2.8728232647,1.035411264,-0.7151261625
C,0,1.8673502689,1.6307872137,0.0852865023
C,0,1.3544681647,0.9175576488,1.1600228443
C,0,1.7565040416,-0.3950853933,1.3790516704
C,0,1.3229771237,2.9820487878,-0.2611283514
H,0,3.0515651958,-2.0124467692,0.7425850269
H,0,4.0959848289,-0.6853217957,-1.095102714
H,0,3.286309782,1.6048277954,-1.5410656738
H,0,0.5787595617,1.3495294955,1.7785759491
H,0,1.3108680826,-0.9699337048,2.1818459873
H,0,1.0285693412,3.5288502907,0.63508463
H,0,0.4237138336,2.851373768,-0.8701578345
H,0,2.0407817988,3.577152935,-0.8256419285
N,0,0.6166164435,-1.442813505,-0.4906263261
O,0,0.3321046087,-2.4669794956,-0.0858249485
O,0,0.5029250915,-0.5982940286,-1.2339380916
F,0,-3.214225774,0.2506481526,0.8071195832
B,0,-1.9607343543,-0.0179918501,0.2809089625
F,0,-1.3445086496,1.1599111643,-0.1739740845
F,0,-1.1262567317,-0.6043831853,1.2665123673
F,0,-2.0486554713,-0.9366111444,-0.7839706881

TS NO2BF4 PCM PURE-M06-2X 2.3272_820767
M062X/6-311G*
E(RM062X) = -900.933402046

Zero-point correction= 0.156838 (Hartree/Particle)
Thermal correction to Energy= 0.171943
Thermal correction to Enthalpy= 0.172887
Thermal correction to Gibbs Free Energy= 0.112635
Sum of electronic and ZPE= -900.776564
Sum of electronic and thermal Energies= -900.761459
Sum of electronic and thermal Enthalpies= -900.760515
Sum of electronic and thermal Free Energies= -900.820767

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 107.896 53.099 126.810

C,0,-1.9044643822,-0.8008658046,1.0364187237
C,0,-1.5095961465,0.446443589,1.5483565094
C,0,-1.9486116838,1.5951673177,0.9325818988
C,0,-2.8345559557,1.5465989707,-0.1698518198

C,0,-3.2872890492,0.3093951323,-0.6229231652
C,0,-2.8323890824,-0.8600775711,-0.0278694826
C,0,-3.2627299954,2.8223426716,-0.8285344634
H,0,-1.565829174,-1.7119757115,1.514449605
H,0,-0.8153748302,0.4883867059,2.3763922977
H,0,-1.6138416625,2.5631904553,1.2899902025
H,0,-3.9841504324,0.2590173476,-1.451340238
H,0,-3.171528379,-1.8253559204,-0.3870753218
H,0,-3.6056852313,3.5433347803,-0.0837237499
H,0,-4.0600982118,2.6543486735,-1.551059017
H,0,-2.4154810325,3.2766632441,-1.3498611488
N,0,-0.4154645765,-0.944789574,-0.7462610577
O,0,-0.2358303599,0.12033448,-1.082011807
O,0,-0.217078547,-2.0607628911,-0.7994152047
F,0,1.0593032055,-0.8269012494,1.2541220009
B,0,2.3660435935,-0.8703170527,0.6842469008
F,0,3.0701450835,0.2665390369,1.0609567935
F,0,3.0117757851,-2.026399935,1.1046100726
F,0,2.1963250647,-0.8939136949,-0.718086529

TS NO2BF4 PCM PURE-M06-2X 2.387_820745
M062X/6-311G*
E(RM062X) = -900.934045808

Zero-point correction= 0.156934 (Hartree/Particle)
Thermal correction to Energy= 0.172037
Thermal correction to Enthalpy= 0.172981
Thermal correction to Gibbs Free Energy= 0.113301
Sum of electronic and ZPE= -900.777112
Sum of electronic and thermal Energies= -900.762009
Sum of electronic and thermal Enthalpies= -900.761065
Sum of electronic and thermal Free Energies= -900.820745

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 107.955 53.135 125.608

C,0,2.7854997738,-1.6997822256,-0.1352851467
C,0,3.6327324203,-0.934404998,-0.9638122363
C,0,3.6264970078,0.4510642606,-0.874427149
C,0,2.782682526,1.0928751939,0.03236097
C,0,1.9737418757,0.313316817,0.8871402397
C,0,1.9906327817,-1.0626815197,0.8288734372
C,0,2.709256927,2.589082452,0.0991166239
H,0,2.7969792092,-2.7814849561,-0.1949708573
H,0,4.2773876252,-1.4340333957,-1.6786039409
H,0,4.2673684387,1.0374756317,-1.5229974933
H,0,1.3214540623,0.8151220052,1.5938619767
H,0,1.3473358477,-1.6514945915,1.4675756804
H,0,1.7790567223,2.9373177459,-0.3593305154

H,0,3.5416002592,3.0560965023,-0.4261817123
H,0,2.7066791615,2.9324656129,1.1351594216
N,0,1.2873072433,-1.3849390543,-1.9663601126
O,0,0.8176882163,-0.3808985556,-1.7633134591
O,0,1.4275730824,-2.3546684929,-2.5309779864
F,0,-2.1934216837,-3.0920386893,-0.0767720342
B,0,-1.139992836,-2.30024487,-0.5000674106
F,0,-1.1179519131,-1.0756682849,0.1757401179
F,0,0.0970796497,-2.9582562277,-0.2731062855
F,0,-1.2205923974,-2.0550223601,-1.8899281277

TS NO2BF4 PCM PURE-M06-2X 3.444_820739
M062X/6-311G*
E(RM062X) = -900.936956537

Zero-point correction= 0.158150 (Hartree/Particle)
Thermal correction to Energy= 0.172803
Thermal correction to Enthalpy= 0.173747
Thermal correction to Gibbs Free Energy= 0.116217
Sum of electronic and ZPE= -900.778806
Sum of electronic and thermal Energies= -900.764154
Sum of electronic and thermal Enthalpies= -900.763209
Sum of electronic and thermal Free Energies= -900.820739

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.435 52.859 121.082

C,0,1.9905369329,-1.1432194098,-1.5561769366
C,0,0.9666255978,-0.2206057925,-1.7792644059
C,0,0.9014608713,0.9318159186,-1.0134760743
C,0,1.8661502208,1.1795673944,-0.0105218727
C,0,2.9186631808,0.2590325096,0.1637478471
C,0,2.9696732974,-0.8988914623,-0.5896044317
C,0,1.8387923501,2.4462947042,0.790749962
H,0,2.0244269843,-2.0581069529,-2.1364420785
H,0,0.2153056877,-0.4143029946,-2.5353083541
H,0,0.1046251245,1.6516859031,-1.1710230325
H,0,3.6642358518,0.4382176767,0.9279691695
H,0,3.7520090635,-1.6225102611,-0.4024158884
H,0,2.2065105446,2.2778323409,1.8050371716
H,0,0.837205576,2.8758378134,0.8391058308
H,0,2.4947051944,3.1871576015,0.3251168359
N,0,0.456004816,-0.253505081,1.3960066797
O,0,0.4671085875,-1.2816219202,0.9436720245
O,0,0.1554955208,0.5588842435,2.1228819069
F,0,2.3099682351,-0.7311536745,2.8439888811
B,0,3.144568775,-1.8789674451,2.6668406142
F,0,2.5118003532,-2.7357572048,1.7566440802
F,0,4.3763107823,-1.4608964641,2.1501766838

F,0,3.3144774523,-2.506459443,3.8944983875

TS NO2BF4 PCM PURE-M06-2X 3.1392_820578
M062X/6-311G*
E(RM062X) = -900.934524532

Zero-point correction= 0.157181 (Hartree/Particle)
Thermal correction to Energy= 0.172131
Thermal correction to Enthalpy= 0.173075
Thermal correction to Gibbs Free Energy= 0.113946
Sum of electronic and ZPE= -900.777344
Sum of electronic and thermal Energies= -900.762393
Sum of electronic and thermal Enthalpies= -900.761449
Sum of electronic and thermal Free Energies= -900.820578

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.014 53.050 124.447

C,0,-3.3366780558,-0.5973561632,0.3432648468
C,0,-2.3068260426,-0.6046035527,1.2700590993
C,0,-1.2300609676,0.3054771788,1.1407197579
C,0,-1.2261902987,1.2932092012,0.1364216559
C,0,-2.2508839072,1.2547562218,-0.7999001496
C,0,-3.2855783638,0.3173939401,-0.7064204223
C,0,-0.1593576434,2.3462318706,0.0798818428
H,0,-4.1562933978,-1.3000911755,0.4228229214
H,0,-2.3055203064,-1.3133155634,2.0912539312
H,0,-0.4280340972,0.2978430153,1.8701514213
H,0,-2.2550298037,1.9708706678,-1.6150482286
H,0,-4.0665752461,0.3155215732,-1.458319046
H,0,0.6261815927,2.1550996524,0.8070711108
H,0,-0.6005003142,3.3250137148,0.2854147476
H,0,0.2982384829,2.381637487,-0.9091515159
N,0,-0.3646482818,-1.4829901688,-0.143768429
O,0,-0.8367787793,-1.3888505208,-1.1644368329
O,0,0.3167583471,-1.9624439405,0.6215347725
F,0,1.8580171704,0.1860735087,1.3541306564
B,0,2.4211552283,0.242083143,0.0623050622
F,0,2.9482045276,1.505918924,-0.1752703885
F,0,3.3916345371,-0.7448228896,-0.0727987487
F,0,1.3710746195,-0.013565124,-0.8701420646

TS NO2BF4 PCM PURE-M06-2X 3.1409_820572
M062X/6-311G*
E(RM062X) = -900.934547624

Zero-point correction= 0.157206 (Hartree/Particle)
Thermal correction to Energy= 0.172155
Thermal correction to Enthalpy= 0.173099

Thermal correction to Gibbs Free Energy= 0.113975
Sum of electronic and ZPE= -900.777342
Sum of electronic and thermal Energies= -900.762393
Sum of electronic and thermal Enthalpies= -900.761449
Sum of electronic and thermal Free Energies= -900.820572

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.029 53.041 124.436

C,0,-3.370588333,-0.6556373104,0.3493715391
C,0,-2.3402104542,-0.6523679232,1.2752980435
C,0,-1.2760115029,0.2729408624,1.1485858232
C,0,-1.2866058276,1.2645103442,0.1481667046
C,0,-2.3124206824,1.216496074,-0.7867533527
C,0,-3.3335535757,0.2644422927,-0.6965083825
C,0,-0.2296417337,2.3271932311,0.0871854573
H,0,-4.1805512367,-1.3697218423,0.4268518764
H,0,-2.329187756,-1.36375597,2.0940346471
H,0,-0.4734330371,0.2738391386,1.8773937984
H,0,-2.3274756862,1.9365768895,-1.5982894792
H,0,-4.1155406103,0.255003632,-1.4473089787
H,0,-0.6895737302,3.3110891632,0.2076256444
H,0,0.2823150152,2.3059220993,-0.8752450568
H,0,0.519713663,2.187719083,0.863039899
N,0,-0.3846453778,-1.4952874088,-0.1447001198
O,0,-0.8619257188,-1.4067051973,-1.1634881764
O,0,0.3071445431,-1.9651282199,0.6171940542
F,0,2.8396580493,1.5808750045,-0.1888375845
B,0,2.3717775299,0.2932108455,0.046393209
F,0,1.332858502,-0.0075522139,-0.8853975514
F,0,3.3875012839,-0.6462969628,-0.0937590685
F,0,1.8135076762,0.2071433886,1.3383310543

TS NO2BF4 PCM PURE-M06-2X 3.055_820543
M062X/6-311G*
E(RM062X) = -900.933591759

Zero-point correction= 0.156954 (Hartree/Particle)
Thermal correction to Energy= 0.172137
Thermal correction to Enthalpy= 0.173081
Thermal correction to Gibbs Free Energy= 0.113049
Sum of electronic and ZPE= -900.776638
Sum of electronic and thermal Energies= -900.761454
Sum of electronic and thermal Enthalpies= -900.760510
Sum of electronic and thermal Free Energies= -900.820543

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.018 53.205 126.350

C,0,-1.8128709796,-0.9661759901,-1.4369061229
C,0,-2.9716093019,-0.7342582824,-0.6976106016
C,0,-3.1084477198,0.458750475,0.0446547894
C,0,-2.1104917238,1.4515209066,0.030192558
C,0,-0.9552590167,1.179838566,-0.6830300585
C,0,-0.8065939897,-0.0174242535,-1.408402822
C,0,-2.3057108206,2.7329623886,0.7911291474
H,0,-1.7052446189,-1.8958700626,-1.978191037
H,0,-3.7642857501,-1.4729947482,-0.6790223216
H,0,-4.0272813908,0.6355776095,0.5961083721
H,0,-0.1471702636,1.9036054963,-0.6897686764
H,0,0.1151405358,-0.191274677,-1.9516274984
H,0,-1.4270414423,3.3729112689,0.7194682186
H,0,-2.5012696874,2.5353262109,1.8476709067
H,0,-3.1634564936,3.2839001123,0.3992857729
N,0,-2.1362866097,-1.0869245663,1.5986018721
O,0,-1.0219982302,-0.9494581471,1.4749079369
O,0,-3.0603406697,-1.4357017304,2.1513541041
F,0,-1.8626753327,-3.2792955561,0.5699564192
B,0,-2.9893657646,-3.9527694726,0.0199673959
F,0,-4.1459835957,-3.3712411126,0.5685977912
F,0,-2.9905017965,-3.7623176152,-1.368296156
F,0,-2.924428338,-5.3025178201,0.3331470099

TS NO2BF4 PCM PURE-M06-2X 2.4184_820386
M062X/6-311G*
E(RM062X) = -900.935155388

Zero-point correction= 0.157396 (Hartree/Particle)
Thermal correction to Energy= 0.172289
Thermal correction to Enthalpy= 0.173233
Thermal correction to Gibbs Free Energy= 0.114769
Sum of electronic and ZPE= -900.777760
Sum of electronic and thermal Energies= -900.762867
Sum of electronic and thermal Enthalpies= -900.761923
Sum of electronic and thermal Free Energies= -900.820386

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.113 53.039 123.047

C,0,2.1902840767,-1.1657337018,-1.2140467939
C,0,1.1209839805,-0.3506208562,-1.6496642157
C,0,0.9459745463,0.9141892759,-1.1130782896
C,0,1.8122109411,1.3837463369,-0.1252783809
C,0,2.9045728667,0.5824030149,0.2667067824
C,0,3.1122019831,-0.6668460286,-0.2858831803
C,0,1.5549816224,2.7098952933,0.5224937977
H,0,2.3324585923,-2.1471724139,-1.652224348

H,0,0.4211432193,-0.7305452373,-2.3847773091
H,0,0.0956563138,1.5141709978,-1.4139484635
H,0,3.5865427599,0.9573307642,1.022310663
H,0,3.956436043,-1.2721154724,0.0208077812
H,0,2.3449459763,2.9813320583,1.2220066779
H,0,0.6027639631,2.6626838771,1.0563978101
H,0,1.4672003704,3.4961121554,-0.2305165776
N,0,0.467960043,-1.7431239342,0.3824408597
O,0,0.5668432277,-0.9643060168,1.1886657608
O,0,0.09477977,-2.7134260593,-0.0683134486
F,0,-1.5914240465,-0.7153143228,-0.3620240376
B,0,-2.0713566007,0.5468568941,0.0959992142
F,0,-1.1431786339,1.0533775506,1.0235788935
F,0,-2.1713396261,1.4134522872,-0.9954392994
F,0,-3.3089423884,0.3696455377,0.7024301037

TS NO2BF4 PCM PURE-M06-2X 2.306_820365
M062X/6-311G*
E(RM062X) = -900.933212549

Zero-point correction= 0.157184 (Hartree/Particle)
Thermal correction to Energy= 0.172295
Thermal correction to Enthalpy= 0.173239
Thermal correction to Gibbs Free Energy= 0.112847
Sum of electronic and ZPE= -900.776028
Sum of electronic and thermal Energies= -900.760918
Sum of electronic and thermal Enthalpies= -900.759973
Sum of electronic and thermal Free Energies= -900.820365

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.117 52.951 127.105

C,0,2.4348138537,-1.3145868312,0.7680728002
C,0,3.344440292,-0.9116576603,-0.2304283759
C,0,3.4188546733,0.4173099464,-0.5709974871
C,0,2.64099661,1.3898634668,0.1041151612
C,0,1.8117776578,0.9942661486,1.1524028843
C,0,1.7080301412,-0.3443001032,1.4939266243
C,0,2.715543961,2.8214194195,-0.3290181604
H,0,2.3731253861,-2.3573071761,1.0566676806
H,0,3.9442603428,-1.6516443078,-0.7456912397
H,0,4.0818317143,0.7381899315,-1.3673700807
H,0,1.2164904472,1.7302964689,1.6787983537
H,0,1.0346067867,-0.6570480575,2.2819587168
H,0,2.2223613955,3.4827971397,0.3816318032
H,0,2.2283256918,2.9397473803,-1.3012899489
H,0,3.7543120223,3.1363122785,-0.4483228357
N,0,0.5403344931,-1.2950610276,-0.5465764378
O,0,0.6098104285,-0.3890126427,-1.2223829897

O,0,0.0489529136,-2.2736739147,-0.2401924816
F,0,-1.0658270744,-0.0364504315,0.9175156755
B,0,-2.281551791,-0.0589040797,0.1738787442
F,0,-2.6503196421,1.2440583607,-0.1422014467
F,0,-2.028268266,-0.7883245756,-1.0079394655
F,0,-3.2669360375,-0.692598733,0.9225165055

TS NO2BF4 PCM PURE-M06-2X 2.2457_820277
M062X/6-311G*
E(RM062X) = -900.934436028

Zero-point correction= 0.157405 (Hartree/Particle)
Thermal correction to Energy= 0.172196
Thermal correction to Enthalpy= 0.173141
Thermal correction to Gibbs Free Energy= 0.114159
Sum of electronic and ZPE= -900.777031
Sum of electronic and thermal Energies= -900.762240
Sum of electronic and thermal Enthalpies= -900.761295
Sum of electronic and thermal Free Energies= -900.820277

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.055 52.527 124.137

C,0,2.1492601033,-0.995536205,1.1494984088
C,0,3.2064409239,-0.411843097,0.4446004345
C,0,2.9935350129,0.7935807323,-0.184211926
C,0,1.7577416558,1.4999035549,-0.0802715647
C,0,0.7389442499,0.9592765523,0.6746676526
C,0,0.9029314715,-0.3069746095,1.2525832274
C,0,1.6031564407,2.8056192441,-0.7959165693
H,0,2.2703147103,-1.9511706324,1.646327824
H,0,4.1582519819,-0.9206156061,0.3662909268
H,0,3.7885526082,1.2360443687,-0.7762579577
H,0,-0.2133938634,1.4652438982,0.77253443
H,0,0.0884773841,-0.735919998,1.8226234546
H,0,0.6087818191,3.2235885092,-0.6484719507
H,0,1.7695882194,2.6700880278,-1.8673194202
H,0,2.3464494045,3.5241040257,-0.4413491174
N,0,0.7232194993,-1.6578364031,-0.4538690311
O,0,0.9951841648,-1.1104999954,-1.4272010844
O,0,0.1965787766,-2.6024581844,-0.0490196378
F,0,-3.7024847419,-0.3303972301,0.0536387594
B,0,-2.4110433849,0.1348622126,0.2638671733
F,0,-2.0083713333,-0.1256626805,1.5900021393
F,0,-1.5136543045,-0.5279093582,-0.6085925905
F,0,-2.3347727981,1.5156048739,0.0275614194

TS NO2BF4 PCM PURE-M06-2X 2.386_820166
M062X/6-311G*

E(RM062X) = -900.934054552

Zero-point correction= 0.157094 (Hartree/Particle)
Thermal correction to Energy= 0.172074
Thermal correction to Enthalpy= 0.173018
Thermal correction to Gibbs Free Energy= 0.113888
Sum of electronic and ZPE= -900.776961
Sum of electronic and thermal Energies= -900.761980
Sum of electronic and thermal Enthalpies= -900.761036
Sum of electronic and thermal Free Energies= -900.820166

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	107.978	53.080	124.449

C,0,2.662863955,-0.9538173389,0.5475773011
C,0,3.3029282193,-0.2085289197,-0.4644461782
C,0,2.9226250564,1.1050014067,-0.7080942142
C,0,1.9069793458,1.6929160432,0.0449535254
C,0,1.3044535926,0.9495578447,1.0837074962
C,0,1.6907066111,-0.3440657983,1.3544920805
C,0,1.4421679335,3.0920416289,-0.228583706
H,0,2.9655347348,-1.9748305725,0.7466419942
H,0,4.0831575053,-0.6713924534,-1.058721438
H,0,3.4059277924,1.6695326624,-1.4973040885
H,0,0.5156744311,1.4106338442,1.6687405269
H,0,1.2046108719,-0.9153445275,2.1328600637
H,0,1.4826084035,3.6928756309,0.6827024038
H,0,0.4016546884,3.0865211929,-0.5638367845
H,0,2.0473338095,3.5765611835,-0.9936278578
N,0,1.2116731408,-1.498052747,-1.2667639288
O,0,1.6323443187,-2.4963794572,-1.591615061
O,0,0.4771571154,-0.6436750417,-1.292070642
F,0,-1.7388376982,-3.6044856516,1.0699230283
B,0,-0.9276647509,-2.6751683606,0.44201542
F,0,-1.2685948854,-1.3690775348,0.808926283
F,0,0.4328088645,-2.8943887564,0.7826354555
F,0,-1.0188460553,-2.7947932776,-0.9635556795

TS NO2BF4 PCM PURE-M06-2X 3.298_819960
M062X/6-311G*
E(RM062X) = -900.933597392

Zero-point correction= 0.157112 (Hartree/Particle)
Thermal correction to Energy= 0.172226
Thermal correction to Enthalpy= 0.173170
Thermal correction to Gibbs Free Energy= 0.113637
Sum of electronic and ZPE= -900.776485
Sum of electronic and thermal Energies= -900.761372
Sum of electronic and thermal Enthalpies= -900.760427

Sum of electronic and thermal Free Energies= -900.819960

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.073 53.194 125.297

C,0,1.8369650052,-1.0828215726,1.50959523
C,0,2.7631935911,-0.8856336433,0.5036692179
C,0,2.7097591776,0.2908534168,-0.2598534037
C,0,1.8022326727,1.3340556048,0.0452037579
C,0,0.8929678583,1.1200321001,1.0756957904
C,0,0.9008663086,-0.0793553906,1.7866185227
C,0,1.8535788962,2.6267445638,-0.7168847224
H,0,1.8234947552,-2.0164969138,2.055947248
H,0,3.4758863137,-1.6603161735,0.2584298039
H,0,3.434609487,0.4424241676,-1.0539498016
H,0,0.1679559223,1.8880603468,1.3209829957
H,0,0.1674532995,-0.2360417389,2.5694560859
H,0,0.9071812932,3.1635814041,-0.6589633827
H,0,2.103611911,2.4635434957,-1.7671940194
H,0,2.632635914,3.2704658426,-0.2994443946
N,0,0.9770984273,-0.6439937116,-1.6440093248
O,0,0.1686128471,-0.9889791838,-0.9447207988
O,0,1.4638342751,-0.4583234501,-2.6487851267
F,0,2.7158560403,-3.8672508421,0.345153912
B,0,1.6924695085,-3.8094075711,-0.6086132158
F,0,0.4897746883,-3.4375407419,0.0051336961
F,0,2.0225867103,-2.8083745081,-1.5737267781
F,0,1.5561700977,-5.0321855006,-1.2548212919

TS NO2BF4 PCM PURE-M06-2X 3.271_819957
M062X/6-311G*
E(RM062X) = -900.933728827

Zero-point correction= 0.157401 (Hartree/Particle)
Thermal correction to Energy= 0.172492
Thermal correction to Enthalpy= 0.173437
Thermal correction to Gibbs Free Energy= 0.113771
Sum of electronic and ZPE= -900.776328
Sum of electronic and thermal Energies= -900.761236
Sum of electronic and thermal Enthalpies= -900.760292
Sum of electronic and thermal Free Energies= -900.819957

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.241 53.059 125.576

C,0,2.0147245719,-1.1252880247,-1.4900910494
C,0,1.059779281,-0.1605400593,-1.8277095093
C,0,0.9893292932,1.0583437247,-1.1519250528

C,0,1.8532627368,1.3305304039,-0.097717552
C,0,2.7767373362,0.3237029595,0.2721494996
C,0,2.8935110742,-0.8725584308,-0.4539638696
C,0,1.840384541,2.6460753052,0.6262318171
H,0,2.0490223134,-2.0756740742,-2.0056122586
H,0,0.3595667283,-0.3626213342,-2.6304979758
H,0,0.249504584,1.7949143758,-1.4453690535
H,0,3.4666407682,0.520425166,1.0873298555
H,0,3.6187333885,-1.6189302322,-0.1603976655
H,0,2.6072867645,3.3046835627,0.2092934368
H,0,2.0670004808,2.5228279179,1.6872041928
H,0,0.8782103481,3.1480084427,0.5279407867
N,0,1.0402862801,-0.6716892205,1.5994317243
O,0,0.2515015489,-1.0137475662,0.8764064625
O,0,1.5002584382,-0.4953444328,2.6184699349
F,0,2.0695001341,-2.8482054502,1.5675773602
B,0,1.7915647562,-3.8281023948,0.5661532857
F,0,0.6136287469,-3.4509722039,-0.0915142729
F,0,2.8572608806,-3.8541359272,-0.3421109865
F,0,1.637840005,-5.0680345077,1.17433589

TS NO2BF4 PCM PURE-M06-2X 2.6887_819594
M062X/6-311G*
E(RM062X) = -900.934845641

Zero-point correction= 0.157950 (Hartree/Particle)
Thermal correction to Energy= 0.172816
Thermal correction to Enthalpy= 0.173760
Thermal correction to Gibbs Free Energy= 0.115252
Sum of electronic and ZPE= -900.776895
Sum of electronic and thermal Energies= -900.762030
Sum of electronic and thermal Enthalpies= -900.761086
Sum of electronic and thermal Free Energies= -900.819594

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.444 52.746 123.141

C,0,-2.3725152963,-1.1840582138,1.1802241997
C,0,-1.1890446447,-0.4904891317,1.5129147256
C,0,-0.9206141857,0.775918181,0.9630481065
C,0,-1.7459657119,1.3018590992,-0.017590935
C,0,-2.8839706831,0.5662604278,-0.3866438966
C,0,-3.2128158336,-0.648680789,0.2211127556
C,0,-1.4179471479,2.6124736492,-0.6756482
H,0,-2.5962376045,-2.1325144265,1.6538465104
H,0,-0.5154102947,-0.8892222495,2.2624521902
H,0,-0.0335371949,1.3120545525,1.2727010583
H,0,-3.5314833868,0.9582404204,-1.165223398
H,0,-4.1115976862,-1.174317721,-0.0768798545

H,0,-2.0526399542,3.410877638,-0.282837663
H,0,-1.5829970548,2.5599411855,-1.7531185418
H,0,-0.3763671507,2.8772813765,-0.4948817359
N,0,-0.1633184527,-1.5387271379,-0.3106456323
O,0,-0.7038767832,-1.203440821,-1.2445621902
O,0,0.6153827433,-2.148982988,0.2413958331
F,0,1.4332237942,0.2326235577,-0.8146430045
B,0,2.2379187357,0.6944580781,0.2628490652
F,0,3.5793278775,0.5381533754,-0.0526262894
F,0,1.9337089097,2.0411034207,0.5017613738
F,0,1.9053370053,-0.0710614835,1.3982605229

TS NO2BF4 PCM PURE-M06-2X 2.586_819521utf00004
M062X/6-311G*
E(RM062X) = -900.932715643

Zero-point correction= 0.157029 (Hartree/Particle)
Thermal correction to Energy= 0.172176
Thermal correction to Enthalpy= 0.173120
Thermal correction to Gibbs Free Energy= 0.113195
Sum of electronic and ZPE= -900.775687
Sum of electronic and thermal Energies= -900.760540
Sum of electronic and thermal Enthalpies= -900.759596
Sum of electronic and thermal Free Energies= -900.819521

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.042 53.172 126.123

C,0,1.7424109949,-1.0657520108,1.2509626052
C,0,2.7843586054,-0.7104945076,0.3685934925
C,0,2.8489304486,0.5801054748,-0.1893436899
C,0,1.8358337633,1.4898172295,0.0507061562
C,0,0.7800296286,1.1021905693,0.9061395654
C,0,0.7391630437,-0.1427605415,1.5163320956
C,0,1.8283761124,2.8573327324,-0.5706790585
H,0,1.7050388707,-2.0546453143,1.689503834
H,0,3.5890493295,-1.4126608398,0.1828232818
H,0,3.681964984,0.8426522415,-0.8317495963
H,0,-0.0224875481,1.8095872037,1.090998154
H,0,-0.0864780378,-0.4181791643,2.1563103693
H,0,1.7478096206,3.6284206805,0.1982193754
H,0,0.9688011846,2.9702436188,-1.2356923683
H,0,2.7346272197,3.0383929924,-1.1474486497
N,0,1.3267839627,-1.5862240304,-1.247554152
O,0,0.4824019787,-0.8475838501,-1.3756090543
O,0,1.9246383344,-2.5007733155,-1.5557900154
F,0,-0.740151014,-2.6698818339,2.1132128465
B,0,-1.1559887508,-2.7578376243,0.7765484202
F,0,-1.577844528,-1.5005471787,0.3233727767

F,0,-0.0409928985,-3.1571200324,-0.0141813447
F,0,-2.1740973046,-3.6940224994,0.6434629565

TS NO2BF4 PCM PURE-M06-2X 2.8006_818867
M062X/6-311G*
E(RM062X) = -900.933304698

Zero-point correction= 0.157588 (Hartree/Particle)
Thermal correction to Energy= 0.172608
Thermal correction to Enthalpy= 0.173552
Thermal correction to Gibbs Free Energy= 0.114438
Sum of electronic and ZPE= -900.775717
Sum of electronic and thermal Energies= -900.760697
Sum of electronic and thermal Enthalpies= -900.759753
Sum of electronic and thermal Free Energies= -900.818867

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.313 52.989 124.415

C,0,-0.3368855723,-1.3350395877,0.4407082457
C,0,-0.6992460203,-0.2460071839,1.2512930834
C,0,-2.0252881806,0.2424587292,1.2539477875
C,0,-2.9735819897,-0.283042188,0.3878985258
C,0,-2.570846589,-1.322223632,-0.4628590138
C,0,-1.278479545,-1.8552288926,-0.4277501787
C,0,-4.3823453643,0.2412282261,0.3359469083
H,0,0.6731575474,-1.7222661924,0.4745503158
H,0,0.0333747258,0.167640295,1.9326837633
H,0,-2.2892859595,1.0523365611,1.9264931589
H,0,-3.2924152948,-1.7328204269,-1.16282063
H,0,-1.0178970767,-2.6708455468,-1.0912182302
H,0,-5.1007313367,-0.5659165994,0.4913084722
H,0,-4.5938581327,0.685383102,-0.6394482506
H,0,-4.5500744977,0.9999129807,1.0999107802
N,0,-0.2978100994,1.3201865102,-0.4490243388
O,0,-0.8309265641,0.9471586756,-1.372092065
O,0,0.3246022042,2.0658022223,0.1313859366
F,0,2.2005819251,0.2936250398,1.0016212795
B,0,2.6736879842,-0.1637901783,-0.2447614792
F,0,2.8133823605,-1.5538729782,-0.2078804074
F,0,1.6950244288,0.1733700799,-1.2220176065
F,0,3.8772160471,0.4496569845,-0.5610520571

TS NO2BF4 PCM PURE-M06-2X 2.801_818858
M062X/6-311G*
E(RM062X) = -900.933304728

Zero-point correction= 0.157591 (Hartree/Particle)
Thermal correction to Energy= 0.172609
Thermal correction to Enthalpy= 0.173553
Thermal correction to Gibbs Free Energy= 0.114446
Sum of electronic and ZPE= -900.775714
Sum of electronic and thermal Energies= -900.760696
Sum of electronic and thermal Enthalpies= -900.759751
Sum of electronic and thermal Free Energies= -900.818858

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.314 52.988 124.401

C,0,-1.3716701134,-0.6558325213,1.2418092285
C,0,-0.9355301892,0.6527453759,1.1479833968
C,0,-1.7042533507,1.6014619389,0.4663799415
C,0,-2.9430290054,1.2851887776,-0.1091750597
C,0,-3.375857617,-0.0301816176,-0.0201096267
C,0,-2.5759558681,-1.0098265211,0.6103670697
C,0,-3.750401349,2.3438372078,-0.8088823159
H,0,-0.7861552695,-1.4097000798,1.7518622925
H,0,0.0069603981,0.9475677583,1.5930847547
H,0,-1.3379677968,2.6207947171,0.3889874731
H,0,-4.3252949637,-0.3233657068,-0.4566037779
H,0,-2.9230196865,-2.0330932838,0.6782408852
H,0,-3.939152002,3.188368415,-0.1434103562
H,0,-4.7101655353,1.9516498371,-1.144157937
H,0,-3.2139527562,2.7263834854,-1.6802526053
N,0,-1.5497085221,-1.2843507278,-1.4815939459
O,0,-1.9819360787,-2.2901398807,-1.7676263971
O,0,-0.926219418,-0.3608712124,-1.6656679411
F,0,0.4172319424,-2.3368186567,-0.5292130986
B,0,0.2064885118,-3.4218460944,0.3678913745
F,0,0.8221677143,-4.5617763407,-0.1284223347
F,0,0.7223587909,-3.0776909855,1.6203375822
F,0,-1.185151836,-3.6194638846,0.4716783974

TS NO2BF4 PCM PURE-M06-2X 2.8758_818627
M062X/6-311G*
E(RM062X) = -900.932099320

Zero-point correction= 0.157024 (Hartree/Particle)
Thermal correction to Energy= 0.171983
Thermal correction to Enthalpy= 0.172927
Thermal correction to Gibbs Free Energy= 0.113472
Sum of electronic and ZPE= -900.775075
Sum of electronic and thermal Energies= -900.760116
Sum of electronic and thermal Enthalpies= -900.759172
Sum of electronic and thermal Free Energies= -900.818627

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 107.921 52.799 125.133

C,0,-0.1779094973,-1.4172019709,0.0343672086
C,0,-1.1399073529,-1.829042212,0.9266388414
C,0,-2.4966567711,-1.4548179549,0.7690119393
C,0,-2.9239379546,-0.6716222814,-0.2867654006
C,0,-1.9349245152,-0.1983408315,-1.1662605582
C,0,-0.5648532458,-0.5608860166,-1.0053518642
C,0,-4.3626490769,-0.2873855503,-0.4821975585
H,0,0.8631472008,-1.6875211945,0.1500799224
H,0,-0.8657456119,-2.4520557157,1.7698008167
H,0,-3.219863819,-1.8029226249,1.498841255
H,0,-2.214635207,0.4274827183,-2.0083514531
H,0,0.177425689,-0.2086557021,-1.710800007
H,0,-5.0048006707,-0.7941554235,0.2367949814
H,0,-4.6981571394,-0.5470015085,-1.4877130002
H,0,-4.4938546384,0.7901111381,-0.3590558006
N,0,-0.8531518506,1.3782220293,0.0226746633
O,0,-1.0573828151,1.1955912709,1.1359391979
O,0,-0.5449167965,2.1773565081,-0.7466933479
F,0,2.3363407419,-0.18952417,-1.303202978
B,0,2.6639364592,0.2522221151,-0.0055172231
F,0,3.7983986387,1.052982433,-0.0421154099
F,0,1.5670819061,0.9971850076,0.4974497674
F,0,2.8681903266,-0.8625200636,0.8185130077

TS NO2BF4 PCM PURE-M06-2X 2.778_818581
M062X/6-311G*
E(RM062X) = -900.931834829

Zero-point correction= 0.157319 (Hartree/Particle)
Thermal correction to Energy= 0.172491
Thermal correction to Enthalpy= 0.173435
Thermal correction to Gibbs Free Energy= 0.113253
Sum of electronic and ZPE= -900.774516
Sum of electronic and thermal Energies= -900.759344
Sum of electronic and thermal Enthalpies= -900.758400
Sum of electronic and thermal Free Energies= -900.818581

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.239 53.065 126.662

C,0,-1.0050072795,0.2799496525,1.5231762953
C,0,-2.2897475524,0.7333179202,1.1771116556
C,0,-3.1695133393,-0.0892267958,0.4405294196
C,0,-2.7467474128,-1.3194120369,-0.0418073752
C,0,-1.4359205739,-1.7217263745,0.2577673947

C,0,-0.5809174981,-0.9458217731,1.0447147868
C,0,-3.6405703038,-2.1891523225,-0.8822337129
H,0,-0.3611461264,0.9133578001,2.1166386597
H,0,-2.6256875557,1.6923191544,1.5516583796
H,0,-4.175294961,0.2617522412,0.2331031748
H,0,-1.0818278089,-2.674571494,-0.1241124013
H,0,0.4168883995,-1.3037606353,1.2671843352
H,0,-3.3492484756,-2.1349772639,-1.9343029912
H,0,-4.6820066867,-1.877475593,-0.8041494876
H,0,-3.5689584979,-3.2334874884,-0.5750855697
N,0,-1.5274760886,1.5818464959,-0.8744236835
O,0,-1.9524229224,2.6278902878,-0.8015344589
O,0,-0.9830037912,0.7424961846,-1.3972316359
F,0,-0.7656106117,3.2347801648,1.6750460703
B,0,0.3290610529,3.5221718034,0.8324563293
F,0,1.4557873991,3.8135856994,1.586682589
F,0,0.5728665241,2.3615691053,0.0401942687
F,0,-0.0051618898,4.5757002677,-0.0169100423

TS NO2BF4 PCM PURE-M06-2X 2.840_818475
M062X/6-311G*
E(RM062X) = -900.931718302

Zero-point correction= 0.157209 (Hartree/Particle)
Thermal correction to Energy= 0.172398
Thermal correction to Enthalpy= 0.173342
Thermal correction to Gibbs Free Energy= 0.113243
Sum of electronic and ZPE= -900.774509
Sum of electronic and thermal Energies= -900.759320
Sum of electronic and thermal Enthalpies= -900.758376
Sum of electronic and thermal Free Energies= -900.818475

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.182 53.116 126.490

C,0,2.6536422561,-0.9929999484,0.5636206246
C,0,3.1583163724,-0.2790537774,-0.533788446
C,0,2.7903488062,1.0732308853,-0.7446874421
C,0,1.8550094252,1.6920344141,0.0771222616
C,0,1.3053652233,0.9305289509,1.1129049969
C,0,1.7044411042,-0.3904685592,1.3623224748
C,0,1.4165626468,3.111746618,-0.1561965167
H,0,2.9526312603,-2.0188128985,0.7208572409
H,0,3.9002928048,-0.739472615,-1.17522762
H,0,3.2355370637,1.6186079521,-1.5712101139
H,0,0.5496719722,1.3799921178,1.74993015
H,0,1.2539937529,-0.9395083454,2.1801515236
H,0,1.3587877725,3.6602110128,0.7849044082
H,0,0.4248420086,3.1379091423,-0.6144528317

H,0,2.1078484278,3.6346071064,-0.816907556
N,0,1.3882615201,-0.6759381156,-1.9586822029
O,0,1.9299163371,-0.8602473875,-2.9394180418
O,0,0.4466342083,-0.6283231276,-1.3335249735
F,0,1.263001083,-4.9893491456,-1.3935587524
B,0,1.2192602327,-3.6070750478,-1.318762625
F,0,0.6827193165,-3.1837656301,-0.0950177196
F,0,2.5219453601,-3.0612089381,-1.4488797693
F,0,0.4384110453,-3.0726466635,-2.3669220696

TS NO2BF4 PCM PURE-M06-2X 3.1393_818379
M062X/6-311G*
E(RM062X) = -900.933595319

Zero-point correction= 0.157755 (Hartree/Particle)
Thermal correction to Energy= 0.172498
Thermal correction to Enthalpy= 0.173442
Thermal correction to Gibbs Free Energy= 0.115216
Sum of electronic and ZPE= -900.775840
Sum of electronic and thermal Energies= -900.761097
Sum of electronic and thermal Enthalpies= -900.760153
Sum of electronic and thermal Free Energies= -900.818379

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.244 52.837 122.548

C,0,-3.3235559084,-0.2403805492,-0.5207739974
C,0,-2.878131179,-0.4202213903,0.777873035
C,0,-1.7576465175,0.3080580222,1.2444675247
C,0,-1.1334059884,1.287473413,0.4484256038
C,0,-1.573265173,1.4174164635,-0.8613523907
C,0,-2.6473680248,0.6606097657,-1.3421372351
C,0,-0.0416549077,2.1461792475,1.0102486085
H,0,-4.1670544932,-0.8043595493,-0.8979606492
H,0,-3.3651893758,-1.1276139754,1.4399434876
H,0,-1.4287666039,0.1753199425,2.2704588066
H,0,-1.070397552,2.1115445318,-1.5244485535
H,0,-2.961715063,0.785062015,-2.3722086451
H,0,0.5920240481,1.5777330943,1.6899725585
H,0,-0.4801871847,2.9804424712,1.5652664955
H,0,0.5886359467,2.5434875651,0.2172970347
N,0,-0.6207997364,-1.5678297531,0.3671568999
O,0,-0.4427956481,-2.1519703977,1.3221083221
O,0,-0.5414729989,-1.392640788,-0.7429983798
F,0,3.1075735489,-0.7572368735,-0.8288008972
B,0,2.2075641028,0.1523688672,-0.2802387995
F,0,1.2794575901,0.5613759927,-1.251374923
F,0,1.4808769465,-0.4958653794,0.7667519857
F,0,2.8742831716,1.2539842641,0.248560108

TS NO2BF4 PCM PURE-M06-2X 3.052_818171
M062X/6-311G*
E(RM062X) = -900.934049352

Zero-point correction= 0.157910 (Hartree/Particle)
Thermal correction to Energy= 0.172527
Thermal correction to Enthalpy= 0.173471
Thermal correction to Gibbs Free Energy= 0.115879
Sum of electronic and ZPE= -900.776140
Sum of electronic and thermal Energies= -900.761522
Sum of electronic and thermal Enthalpies= -900.760578
Sum of electronic and thermal Free Energies= -900.818171

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.262 52.647 121.214

C,0,-2.0181286716,-0.8468271888,0.9555131106
C,0,-1.6402772598,0.3403913135,1.560641443
C,0,-1.9393753415,1.5838888026,0.9377283154
C,0,-2.7216159469,1.6446499021,-0.2349822198
C,0,-3.031913573,0.4407471178,-0.8467852106
C,0,-2.6785896645,-0.786957826,-0.267866971
C,0,-3.1923868878,2.9447625539,-0.8136126851
H,0,-1.7791202651,-1.7993055535,1.410227589
H,0,-1.095400059,0.3375228295,2.4981566861
H,0,-1.6585097821,2.5061636442,1.4346387603
H,0,-3.5724940355,0.4465373266,-1.7871405767
H,0,-2.9410668403,-1.7056743798,-0.7800439302
H,0,-2.8035105569,3.7946793524,-0.2580998679
H,0,-4.2845249974,2.9773338918,-0.7976009777
H,0,-2.8593735506,3.0307424419,-1.8480032587
N,0,0.108966335,1.1443588073,0.0483651966
O,0,-0.0578730115,0.5087311552,-0.8768731349
O,0,0.8188603814,1.7278017798,0.7232453318
F,0,-0.3925887379,3.4520015409,-0.8820192319
B,0,0.1188944672,3.1751291378,-2.1789862943
F,0,-0.8057059113,2.3583064451,-2.8462615761
F,0,0.3327833907,4.3556798092,-2.8715444557
F,0,1.3233685183,2.4675180963,-2.0050560421

TS NO2BF4 PCM PURE-M06-2X 2.8774_817851
M062X/6-311G*
E(RM062X) = -900.932123346

Zero-point correction= 0.157359 (Hartree/Particle)
Thermal correction to Energy= 0.172184
Thermal correction to Enthalpy= 0.173128
Thermal correction to Gibbs Free Energy= 0.114273

Sum of electronic and ZPE= -900.774764
Sum of electronic and thermal Energies= -900.759940
Sum of electronic and thermal Enthalpies= -900.758995
Sum of electronic and thermal Free Energies= -900.817851

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.047 52.687 123.871

C,0,-0.3055309097,-1.4444425884,0.1370791381
C,0,-0.6115834833,-0.4254350119,1.0486605156
C,0,-1.9272315792,0.1241594451,1.0977238567
C,0,-2.939842152,-0.3258666099,0.2333320532
C,0,-2.5845063842,-1.2828833579,-0.6988622072
C,0,-1.2835875774,-1.8401003712,-0.745432729
C,0,-4.3181523552,0.2673574912,0.2988033963
H,0,0.6945296209,-1.8557263555,0.1049316704
H,0,0.1461144674,-0.0859021541,1.7438543201
H,0,-2.1508991025,0.877995239,1.8462648629
H,0,-3.3234743013,-1.6273199814,-1.4146660261
H,0,-1.065533034,-2.5926918708,-1.4939810742
H,0,-4.6509520787,0.3671814151,1.3328006572
H,0,-5.0363326954,-0.3506460587,-0.2385355459
H,0,-4.3258020872,1.264163608,-0.1496116754
N,0,-0.6136173513,1.3953869915,-0.2095120296
O,0,-0.7977603067,1.1047936613,-1.3034263137
O,0,-0.2337305848,2.2392742779,0.4755843079
F,0,2.2998382808,-0.3985605098,1.458161478
B,0,2.7274466814,-0.1521117369,0.137985622
F,0,2.8124761883,-1.3702837741,-0.5492515457
F,0,1.7558268031,0.6631999027,-0.4963372508
F,0,3.954967941,0.4980163488,0.1435545189

TS NO2BF4 PCM PURE-M06-2X 2.776_817301utf00003
M062X/6-311G*
E(RM062X) = -900.930633255

Zero-point correction= 0.157417 (Hartree/Particle)
Thermal correction to Energy= 0.172413
Thermal correction to Enthalpy= 0.173357
Thermal correction to Gibbs Free Energy= 0.113332
Sum of electronic and ZPE= -900.773216
Sum of electronic and thermal Energies= -900.758220
Sum of electronic and thermal Enthalpies= -900.757276
Sum of electronic and thermal Free Energies= -900.817301

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.191 52.726 126.334

C,0,-1.8289284203,-0.7657565707,0.8939667526
C,0,-1.4292142008,0.4485207917,1.3975171205
C,0,-1.9517626803,1.6414831128,0.8645165234
C,0,-2.9136562163,1.6572448101,-0.1499626209
C,0,-3.3041000821,0.431850542,-0.6711649732
C,0,-2.7127591118,-0.7792905041,-0.2066267225
C,0,-3.4703526618,2.9556427973,-0.6640412538
H,0,-1.4275799058,-1.6971950941,1.2662599702
H,0,-0.7085015585,0.4999820375,2.2038956141
H,0,-1.6042883109,2.5879927841,1.2670138431
H,0,-4.0342218903,0.3834111453,-1.4726784629
H,0,-3.0673643874,-1.7274021091,-0.5905436444
H,0,-3.8157326455,3.5810648612,0.1603405897
H,0,-4.3068703483,2.7860989398,-1.3409505379
H,0,-2.7022737068,3.5139037561,-1.2037152014
N,0,-1.3137299306,-0.4556674069,-1.8166460622
O,0,-0.4747100387,0.2393009622,-1.4720308649
O,0,-1.7207921734,-1.0954022849,-2.6756956276
F,0,-0.4826909172,-2.6022484646,-0.7816522722
B,0,0.7056052131,-2.8983295438,-1.5121423529
F,0,1.7881076479,-2.9054288473,-0.6376427995
F,0,0.5621302065,-4.1318240879,-2.139139272
F,0,0.8669431193,-1.8811706269,-2.4736527452

Pi Complexes for Toluene + $NO_2^+BF_4^-$ M062X/6-311G*/PCM(CH_2Cl_2)
Pi Complex NO2BF4 PCM PURE-M06-2X 2.896_825610
M062X/6-311G*
E(RM062X) = -900.938583160

Zero-point correction= 0.157970 (Hartree/Particle)
Thermal correction to Energy= 0.173870
Thermal correction to Enthalpy= 0.174814
Thermal correction to Gibbs Free Energy= 0.112973
Sum of electronic and ZPE= -900.780613
Sum of electronic and thermal Energies= -900.764713
Sum of electronic and thermal Enthalpies= -900.763769
Sum of electronic and thermal Free Energies= -900.825610

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	109.105	54.829	130.156

C,0,-3.2836712936,-3.3582062958,-0.449190649
C,0,-3.9330774419,-2.9881248327,-1.6263685303
C,0,-3.2454164433,-3.010560022,-2.8383459772
C,0,-1.9063866986,-3.4040773131,-2.8933543143
C,0,-1.2704718,-3.783830116,-1.7073939679
C,0,-1.9455065851,-3.7574682186,-0.4940817299
C,0,-1.1302674297,-3.3984087368,-4.1820879906
H,0,-3.8165708741,-3.3412325678,0.4954529982

H,0,-4.9735623575,-2.6837983356,-1.5998906655
H,0,-3.7537271621,-2.7102135931,-3.7492115684
H,0,-0.2235867247,-4.0609200392,-1.7263104317
H,0,-1.4211641046,-4.0310882905,0.4138746319
H,0,-1.7245397998,-3.0149967227,-5.0117764418
H,0,-0.7973010016,-4.406915915,-4.4384815515
H,0,-0.2364965291,-2.7785092305,-4.0773093117
N,0,-2.0461247957,-0.7397862508,-0.4447840209
O,0,-2.4720632102,-0.5726430738,0.5663572785
O,0,-1.6601406985,-0.8129227261,-1.4775979773
F,0,2.1723628474,-1.2237550177,0.2454487076
B,0,1.0572297089,-1.9136897121,-0.2057501149
F,0,0.8232240511,-1.6443513963,-1.5630868136
F,0,1.1951586826,-3.2839813721,0.0055679402
F,0,-0.0934391401,-1.4547164216,0.5224070001

Pi Complex NO2BF4 PCM PURE-M06-2X 2.910_824610
M062X/6-311G*
E(RM062X) = -900.938478053

Zero-point correction= 0.158515 (Hartree/Particle)
Thermal correction to Energy= 0.174305
Thermal correction to Enthalpy= 0.175249
Thermal correction to Gibbs Free Energy= 0.113868
Sum of electronic and ZPE= -900.779963
Sum of electronic and thermal Energies= -900.764173
Sum of electronic and thermal Enthalpies= -900.763229
Sum of electronic and thermal Free Energies= -900.824610

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.378 54.646 129.186

C,0,-0.8391229782,-0.0056112486,1.3390893934
C,0,-1.9779336709,0.7705402966,1.1263326469
C,0,-3.0518627151,0.2605016238,0.3945930617
C,0,-3.0091224776,-1.0324639307,-0.1267477319
C,0,-1.8603499394,-1.8030910042,0.0979668378
C,0,-0.7855957315,-1.2992883781,0.8189471044
C,0,-4.1615256433,-1.6031429336,-0.9100092195
H,0,0.0050781194,0.3878624286,1.8912817371
H,0,-2.0314610951,1.7754681313,1.5328262084
H,0,-3.9331785141,0.8737111352,0.2354607317
H,0,-1.8125411077,-2.8097330069,-0.3067214644
H,0,0.1086437177,-1.8919615648,0.9667248976
H,0,-3.8381611092,-1.9272620932,-1.901857151
H,0,-4.9614024723,-0.8727218581,-1.0329364628
H,0,-4.5758804664,-2.4777702365,-0.4030295529
N,0,-0.3126887202,1.2360925935,-1.239618166
O,0,-0.7108438784,0.3456085483,-1.7638660636

O,0,0.0492179327,2.1858788309,-0.8004106088
F,0,1.6329973486,0.0983181963,-0.7495039287
B,0,2.3814002505,0.3962346161,0.4397277516
F,0,1.8644994432,1.5944154415,0.9585034396
F,0,2.1953962769,-0.6394493273,1.352713726
F,0,3.7181454307,0.5408087403,0.1065718133

Pi Complex NO2BF4 PCM PURE-M06-2X 2.924_825224
M062X/6-311G*
E(RM062X) = -900.938771871

Zero-point correction= 0.158242 (Hartree/Particle)
Thermal correction to Energy= 0.174070
Thermal correction to Enthalpy= 0.175015
Thermal correction to Gibbs Free Energy= 0.113548
Sum of electronic and ZPE= -900.780530
Sum of electronic and thermal Energies= -900.764702
Sum of electronic and thermal Enthalpies= -900.763757
Sum of electronic and thermal Free Energies= -900.825224

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.231 54.755 129.368

C,0,2.7352194338,-0.1304843549,-2.2094330029
C,0,1.6567446806,0.7596443271,-2.1996293365
C,0,1.678766639,1.889025515,-3.0078280212
C,0,2.7769403513,2.1622083204,-3.829446413
C,0,3.8461826708,1.2639876354,-3.8361367146
C,0,3.8278444161,0.122655279,-3.0358033727
C,0,2.7914487912,3.4180722661,-4.6569011295
H,0,2.7171969376,-1.0167171743,-1.5841048285
H,0,0.8046815371,0.5798449339,-1.5534609641
H,0,0.8522867608,2.5884853141,-2.9707743531
H,0,4.7063335911,1.4617755623,-4.4678929841
H,0,4.6650093005,-0.5661021577,-3.0556649425
H,0,1.9913162175,3.4008875805,-5.4008697131
H,0,3.7392595641,3.5454252812,-5.1804538588
H,0,2.6230378113,4.2853037056,-4.0149323935
N,0,3.668908819,1.9091119825,-0.3340100997
O,0,3.9301177526,2.6328194672,-1.1271794105
O,0,3.4990440812,1.1890789443,0.4929116681
F,0,2.0485467083,4.4409382564,-1.4852247969
B,0,1.1187309046,4.0494620953,-0.5084303862
F,0,0.8885411818,5.0828140162,0.3870480537
F,0,-0.0666188763,3.6230519909,-1.1009185959
F,0,1.6946426259,2.9419955133,0.2039746953

Pi Complex NO2BF4 PCM PURE-M06-2X 2.926_823642
M062X/6-311G*

E(RM062X) = -900.935838798

Zero-point correction= 0.158157 (Hartree/Particle)
Thermal correction to Energy= 0.174117
Thermal correction to Enthalpy= 0.175062
Thermal correction to Gibbs Free Energy= 0.112197
Sum of electronic and ZPE= -900.777682
Sum of electronic and thermal Energies= -900.761721
Sum of electronic and thermal Enthalpies= -900.760777
Sum of electronic and thermal Free Energies= -900.823642

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.260 54.776 132.310

C,0,1.21426707,-0.726423966,-0.0955206888
C,0,1.26064487,-0.702760051,-1.4892784935
C,0,2.2092316667,0.0797004851,-2.1391323275
C,0,3.1286393195,0.8480643269,-1.4157736072
C,0,3.071275743,0.8148563594,-0.0214792553
C,0,2.1231639982,0.0372475425,0.6388866032
C,0,4.1317225748,1.7172272004,-2.1263517625
H,0,0.4818346577,-1.3418124536,0.4157687981
H,0,0.5606723583,-1.2964194506,-2.0662700882
H,0,2.2416311426,0.0952615186,-3.2241409068
H,0,3.7649524372,1.4153522498,0.5572917973
H,0,2.0822399455,0.0431659828,1.7216118158
H,0,3.7142670727,2.7102133533,-2.3159088638
H,0,4.4151829309,1.2897311829,-3.0891246983
H,0,5.0336850175,1.8492571683,-1.5276222973
N,0,-0.0305975671,1.90986738,0.1553777345
O,0,0.4827824027,2.3029373936,-0.7431713327
O,0,-0.6352804286,1.536435739,1.004965505
F,0,1.8812408299,3.6705911835,3.6966840241
B,0,1.0356213523,2.9255694616,2.899053691
F,0,1.0646933237,1.5685836914,3.243322115
F,0,-0.2802332674,3.393399272,2.9572951358
F,0,1.4566257501,3.0259591303,1.5282075021

Pi Complex NO2BF4 PCM PURE-M06-2X 2.926_826511
M062X/6-311G*
E(RM062X) = -900.938742887

Zero-point correction= 0.158036 (Hartree/Particle)
Thermal correction to Energy= 0.173959
Thermal correction to Enthalpy= 0.174903
Thermal correction to Gibbs Free Energy= 0.112232
Sum of electronic and ZPE= -900.780707
Sum of electronic and thermal Energies= -900.764784
Sum of electronic and thermal Enthalpies= -900.763840

Sum of electronic and thermal Free Energies= -900.826511

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.161 54.792 131.902

C,0,2.3465828886,-0.8227353157,1.1049569725
C,0,3.1080333345,-0.1788507984,0.1319045298
C,0,2.6714292673,1.0304251606,-0.4065786587
C,0,1.4759099615,1.6150869326,0.0176164275
C,0,0.727538684,0.9664709639,1.0048439972
C,0,1.1524246995,-0.2420025806,1.5421990156
C,0,0.9681914362,2.9003775937,-0.5758847503
H,0,2.6816833013,-1.7644696721,1.5263894756
H,0,4.0397778114,-0.6175826233,-0.2071728968
H,0,3.2641448862,1.5213316601,-1.1719327818
H,0,-0.2154625391,1.3922127201,1.3265798823
H,0,0.5465260592,-0.7376684062,2.2925143588
H,0,-0.0418832789,2.7558799036,-0.9653817083
H,0,1.609702886,3.2527915386,-1.3839633636
H,0,0.9169425699,3.6838553292,0.1840863153
N,0,0.4565728896,-1.7175072605,-0.9417182232
O,0,0.4878473059,-2.7328757618,-0.4951584937
O,0,0.4528326774,-0.7472223097,-1.4702841906
F,0,-1.5275539577,-1.3348756233,0.1433700296
B,0,-2.2936234414,-0.1235466319,0.0457149657
F,0,-2.3587358654,0.4601479337,1.3072964616
F,0,-1.6230819213,0.7194117908,-0.8555555084
F,0,-3.5585476546,-0.4347965433,-0.4294628561

Pi Complex NO2BF4 PCM PURE-M06-2X 2.957_824442
M062X/6-311G*
E(RM062X) = -900.938601018

Zero-point correction= 0.158570 (Hartree/Particle)
Thermal correction to Energy= 0.174297
Thermal correction to Enthalpy= 0.175241
Thermal correction to Gibbs Free Energy= 0.114159
Sum of electronic and ZPE= -900.780031
Sum of electronic and thermal Energies= -900.764304
Sum of electronic and thermal Enthalpies= -900.763360
Sum of electronic and thermal Free Energies= -900.824442

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.373 54.649 128.558

C,0,-1.7332104415,2.2215669955,1.7371988918
C,0,-1.9456793581,2.7401531656,0.459893556
C,0,-2.6815965404,2.0140648168,-0.4706782204

C,0,-3.2214442682,0.7636644264,-0.1468238104
C,0,-2.999571735,0.2542956791,1.1331988998
C,0,-2.2619935202,0.9735679987,2.071184177
C,0,-4.0332531681,-0.0050096355,-1.1554114374
H,0,-1.1659757363,2.7868866532,2.4688614635
H,0,-1.5369436933,3.707703247,0.1909027504
H,0,-2.8376005375,2.4187969571,-1.4658914748
H,0,-3.3768886441,-0.7250101414,1.4038058866
H,0,-2.0915186865,0.5473753518,3.0529193376
H,0,-3.6702508092,0.1644768565,-2.1704269213
H,0,-5.0798020807,0.3102703726,-1.1238346407
H,0,-4.0049011742,-1.0760535288,-0.9518372656
N,0,0.2703393513,0.2515579558,0.8142582657
O,0,-0.2322195726,0.1449373469,-0.1665347023
O,0,0.8572848817,0.3908894159,1.74282759
F,0,-0.6471226207,-1.745894831,1.5003428805
B,0,-0.8903074543,-2.0193304843,2.8892827157
F,0,-0.2561243056,-1.0025762238,3.6216624029
F,0,-2.2639616279,-1.9871127871,3.1161835187
F,0,-0.3575426587,-3.2590656069,3.2032373369

Pi Complex NO2BF4 PCM PURE-M06-2X 2.962_827214
M062X/6-311G*
E(RM062X) = -900.939496146

Zero-point correction= 0.158066 (Hartree/Particle)
Thermal correction to Energy= 0.173974
Thermal correction to Enthalpy= 0.174918
Thermal correction to Gibbs Free Energy= 0.112282
Sum of electronic and ZPE= -900.781430
Sum of electronic and thermal Energies= -900.765522
Sum of electronic and thermal Enthalpies= -900.764578
Sum of electronic and thermal Free Energies= -900.827214

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.170 54.792 131.830

C,0,-1.8926823304,0.7570944744,1.1929573165
C,0,-2.7680908276,0.8457076028,0.1119390401
C,0,-3.1916857089,-0.3101938274,-0.5441960334
C,0,-2.7562222099,-1.569017919,-0.128495171
C,0,-1.882753833,-1.6432517733,0.9633093712
C,0,-1.4511279966,-0.4957349726,1.6166809138
C,0,-3.1935898385,-2.8206258651,-0.8418134216
H,0,-1.554361627,1.6527109381,1.7014886451
H,0,-3.1275105592,1.8147681804,-0.2177435851
H,0,-3.8753788184,-0.2298902965,-1.3833087446
H,0,-1.5337892348,-2.6153808458,1.2975909819
H,0,-0.7580324296,-0.5719035915,2.4457155098

H,0,-2.3810434608,-3.222118406,-1.4533892842
H,0,-4.0429218754,-2.6273299602,-1.497625948
H,0,-3.4787434854,-3.5978480837,-0.1304217338
N,0,-0.0433470306,0.7682775097,-1.121074141
O,0,-0.0567797256,-0.3364495691,-1.1295905147
O,0,-0.068100253,1.8728341562,-1.1891064911
F,0,2.3539587381,0.7913606372,-1.0729514301
B,0,2.5436592718,0.8679907241,0.3381662503
F,0,3.248337448,-0.2352041298,0.7803639014
F,0,3.1713056378,2.0550775648,0.6651416024
F,0,1.2239071489,0.8529394522,0.8900399662

Pi Complex NO2BF4 PCM PURE-M06-2X 2.967_827913
M062X/6-311G*
E(RM062X) = -900.939513201

Zero-point correction= 0.157785 (Hartree/Particle)
Thermal correction to Energy= 0.173822
Thermal correction to Enthalpy= 0.174766
Thermal correction to Gibbs Free Energy= 0.111600
Sum of electronic and ZPE= -900.781729
Sum of electronic and thermal Energies= -900.765692
Sum of electronic and thermal Enthalpies= -900.764747
Sum of electronic and thermal Free Energies= -900.827913

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.075 54.880 132.943

C,0,-0.8792678267,0.2885987742,2.1943375495
C,0,-1.1468714583,1.6567404249,2.2347131334
C,0,-2.4487010063,2.1155662079,2.0802236835
C,0,-3.5105355496,1.2254640016,1.8759978243
C,0,-3.2314433401,-0.140713614,1.8363109025
C,0,-1.9269387274,-0.6091886836,1.9984628894
C,0,-4.9122976405,1.7458905372,1.6995286597
H,0,0.1370560625,-0.0701426295,2.3106718577
H,0,-0.335669918,2.3619572484,2.3693692215
H,0,-2.6497120115,3.1821174072,2.1088829722
H,0,-4.0397213372,-0.8487920488,1.6844512864
H,0,-1.7311956866,-1.6760006585,1.9760346202
H,0,-5.2101669849,2.353750908,2.556714131
H,0,-5.6300853384,0.9323657418,1.5935532372
H,0,-4.9828455927,2.3801410941,0.8124915892
N,0,-1.1234190832,0.2156866337,-0.7620187453
O,0,-1.7940314777,1.0930294935,-0.7229100073
O,0,-0.5177779708,-0.7083369839,-0.8315125563
F,0,1.2217926894,3.2516081533,-1.6071426508
B,0,1.2349072458,1.876076445,-1.4784637652
F,0,0.7822014866,1.507864282,-0.1720175957

F,0,0.2902261793,1.2941732018,-2.3739870894
F,0,2.4890095864,1.3415470636,-1.7037910481

Pi Complex NO2BF4 PCM PURE-M06-2X 2.967_828376
M062X/6-311G*
E(RM062X) = -900.939491139

Zero-point correction= 0.157703 (Hartree/Particle)
Thermal correction to Energy= 0.173810
Thermal correction to Enthalpy= 0.174754
Thermal correction to Gibbs Free Energy= 0.111115
Sum of electronic and ZPE= -900.781788
Sum of electronic and thermal Energies= -900.765681
Sum of electronic and thermal Enthalpies= -900.764737
Sum of electronic and thermal Free Energies= -900.828376

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.067 54.912 133.941

C,0,-1.4241206998,0.1096301571,-2.2712020279
C,0,-1.0048165116,1.3721750192,-1.8526333958
C,0,0.2526737636,1.5348210442,-1.2860170243
C,0,1.1175776022,0.4459655007,-1.1183688845
C,0,0.6880090287,-0.8122427259,-1.5403482096
C,0,-0.5713312395,-0.9816160605,-2.1171659408
C,0,2.4720536506,0.6432817799,-0.4911955469
H,0,-2.4069928887,-0.018464522,-2.7101740615
H,0,-1.6681642037,2.2226280071,-1.9533922653
H,0,0.5714111504,2.5195580755,-0.9582650008
H,0,1.3436141591,-1.6693811673,-1.4252870755
H,0,-0.8835735614,-1.966107039,-2.4491185101
H,0,3.0512661303,1.3845414275,-1.0461908295
H,0,3.0412306337,-0.2861096914,-0.4691277531
H,0,2.3763447295,1.0084563928,0.5342379816
N,0,-1.9833159585,-0.7659445061,0.5076497662
O,0,-1.2284795385,-0.0472299568,0.8745820575
O,0,-2.6899673085,-1.5481543459,0.1695174788
F,0,-3.6342052871,0.1170242244,2.009215534
B,0,-4.2386726053,1.0670471527,1.1340082195
F,0,-5.5599867215,0.7289830285,0.9124581186
F,0,-4.1045256447,2.3398498973,1.654570079
F,0,-3.503664079,0.964061608,-0.0887707093

Pi Complex NO2BF4 PCM PURE-M06-2X 2.976_825066
M062X/6-311G*
E(RM062X) = -900.938818196

Zero-point correction= 0.158520 (Hartree/Particle)
Thermal correction to Energy= 0.174296

Thermal correction to Enthalpy= 0.175240
Thermal correction to Gibbs Free Energy= 0.113752
Sum of electronic and ZPE= -900.780299
Sum of electronic and thermal Energies= -900.764522
Sum of electronic and thermal Enthalpies= -900.763578
Sum of electronic and thermal Free Energies= -900.825066

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.372 54.648 129.412

C,0,2.5238069617,-6.4141808544,1.3577215451
C,0,1.6962834247,-6.4848772171,2.4787747398
C,0,0.520225852,-5.7433421622,2.5216030949
C,0,0.1458827331,-4.9191323061,1.4535879027
C,0,0.9756847229,-4.8644649354,0.3334056863
C,0,2.1553870472,-5.6029995549,0.2834140508
C,0,-1.0999876073,-4.0804744334,1.5324506919
H,0,3.4394014152,-6.9942024093,1.3162924931
H,0,1.9685614341,-7.1178836232,3.3157137712
H,0,-0.1167933331,-5.7979843899,3.3993969584
H,0,0.7155770226,-4.2129480716,-0.4926320423
H,0,2.7909962453,-5.5383002277,-0.5932196762
H,0,-1.3610209399,-3.6737698366,0.5554054914
H,0,-0.944761205,-3.2346281125,2.2060548368
H,0,-1.944150112,-4.6620087253,1.9085498917
N,0,3.4373351044,-3.6693987223,2.0550260238
O,0,4.4523873489,-3.8874744305,1.6625897454
O,0,2.4708179009,-3.4301088694,2.5340087553
F,0,1.1415242903,-2.0271274013,-1.1857713399
B,0,1.8283374655,-1.6596435684,-0.0331384829
F,0,1.0228633406,-1.8454272948,1.1002815907
F,0,2.9716246311,-2.5182264207,0.1175217433
F,0,2.2694758566,-0.3465780329,-0.1076227713

Pi Complex NO2BF4 PCM PURE-M06-2X 2.984_825092
M062X/6-311G*
E(RM062X) = -900.939279115

Zero-point correction= 0.158620 (Hartree/Particle)
Thermal correction to Energy= 0.174375
Thermal correction to Enthalpy= 0.175319
Thermal correction to Gibbs Free Energy= 0.114187
Sum of electronic and ZPE= -900.780659
Sum of electronic and thermal Energies= -900.764904
Sum of electronic and thermal Enthalpies= -900.763960
Sum of electronic and thermal Free Energies= -900.825092

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K

Total 109.422 54.686 128.664

C,0,-2.8901881826,-3.0169865693,1.8699326549
C,0,-2.7571169167,-4.254218692,1.2405703078
C,0,-3.80237106,-5.1719597794,1.2811462844
C,0,-4.9993939706,-4.8789900628,1.9462353939
C,0,-5.1242104146,-3.6342251845,2.5651496127
C,0,-4.0809062162,-2.7112674118,2.5308420598
C,0,-6.1112403308,-5.8899349732,2.0158014315
H,0,-2.0836822001,-2.2929379454,1.8315914097
H,0,-1.8402237484,-4.5008492522,0.7170364045
H,0,-3.689445407,-6.1340393037,0.7902897787
H,0,-6.0346195812,-3.3989533078,3.1027172341
H,0,-4.2006255383,-1.7493524816,3.0186050979
H,0,-6.2542698578,-6.3858810736,1.0538394879
H,0,-7.0468727572,-5.4200434775,2.3174249237
H,0,-5.8763815435,-6.6482841608,2.7650900151
N,0,-2.7102223369,-4.1825991501,4.6105905198
O,0,-2.9380811335,-5.172162047,4.1757434619
O,0,-2.391925215,-3.2270987534,5.0769560989
F,0,-4.8008740545,-3.9268387966,5.5601490713
B,0,-5.76129263,-4.9927088939,5.6134630403
F,0,-6.0550257803,-5.2600736611,6.9426989179
F,0,-6.9018108293,-4.6059509529,4.9161662542
F,0,-5.1680344957,-6.1094124692,5.0060125388

Pi Complex NO2BF4 PCM PURE-M06-2X 2.984_829231
M062X/6-311G*
E(RM062X) = -900.939542391

Zero-point correction= 0.157751 (Hartree/Particle)
Thermal correction to Energy= 0.173888
Thermal correction to Enthalpy= 0.174832
Thermal correction to Gibbs Free Energy= 0.110311
Sum of electronic and ZPE= -900.781792
Sum of electronic and thermal Energies= -900.765654
Sum of electronic and thermal Enthalpies= -900.764710
Sum of electronic and thermal Free Energies= -900.829231

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.117 54.866 135.796

C,0,0.626289451,1.1962856375,-3.3156390777
C,0,0.5934255513,2.39876298,-2.6096558874
C,0,1.6669726207,2.7652576813,-1.8016182993
C,0,2.7880884421,1.9425416678,-1.6824691954
C,0,2.809659495,0.7393438006,-2.3964331737
C,0,1.741343352,0.3656348343,-3.204834599
C,0,3.9305217623,2.3184795469,-0.777028883

H,0,-0.2042231634,0.9137837242,-3.9535866522
H,0,-0.2685358345,3.0526771638,-2.6848161973
H,0,1.6218712632,3.6940519806,-1.2436216481
H,0,3.6740275739,0.0876189583,-2.3146105908
H,0,1.778890838,-0.5689085696,-3.7530102919
H,0,3.8104288042,1.8508066652,0.2042999258
H,0,3.9760126032,3.3971850657,-0.6244875506
H,0,4.8858804402,1.9858879487,-1.1856481693
N,0,-0.4096416833,0.4528442336,-0.6183067978
O,0,-1.4404396754,0.5172019828,-1.0165762822
O,0,0.6198330307,0.3096332338,-0.2428274961
F,0,-0.5699255403,2.6346010746,0.3203308658
B,0,-1.05020931,2.2946081313,1.6243483478
F,0,-1.2032912586,0.8774763194,1.6038120265
F,0,-0.1118119884,2.6524666935,2.5736289484
F,0,-2.273237974,2.8978087457,1.8442933771

Pi Complex NO2BF4 PCM PURE-M06-2X 2.991_828973
M062X/6-311G*
E(RM062X) = -900.939538161

Zero-point correction= 0.157822 (Hartree/Particle)
Thermal correction to Energy= 0.173955
Thermal correction to Enthalpy= 0.174899
Thermal correction to Gibbs Free Energy= 0.110565
Sum of electronic and ZPE= -900.781716
Sum of electronic and thermal Energies= -900.765583
Sum of electronic and thermal Enthalpies= -900.764639
Sum of electronic and thermal Free Energies= -900.828973

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.158 54.844 135.402

C,0,-2.2846922853,1.1676504653,1.4597929793
C,0,-3.2071065298,1.0801158566,0.4178057222
C,0,-3.3315187322,-0.1026557348,-0.304438115
C,0,-2.542085334,-1.2175740526,-0.0041628226
C,0,-1.6178945588,-1.115603827,1.0375597966
C,0,-1.4886051467,0.0635711221,1.7663635225
C,0,-2.695497793,-2.5021755474,-0.7739446432
H,0,-2.1902510708,2.0853062674,2.0303269711
H,0,-3.8283964112,1.933169079,0.1695889733
H,0,-4.0483741795,-0.1613116511,-1.1175009384
H,0,-0.9765774777,-1.9589170769,1.2693700754
H,0,-0.7604142065,0.1210112679,2.568044096
H,0,-3.0464581501,-2.3175729813,-1.7900783893
H,0,-3.4247876224,-3.1548547945,-0.2863085816
H,0,-1.7514842576,-3.0458046151,-0.8282431255
N,0,0.0551530432,1.3787157475,-0.3918199672

O,0,-0.4555257844,0.7470539884,-1.1409894742
O,0,0.5309927992,2.0763896264,0.3238003972
F,0,3.6144279388,-0.1603845663,0.2884250529
B,0,2.4583943733,-0.3696154309,-0.4386920086
F,0,2.1960225106,0.7584846628,-1.2704136915
F,0,2.5245952173,-1.515980863,-1.2077244366
F,0,1.3368856578,-0.4468449426,0.4457216071

Pi Complex NO2BF4 PCM PURE-M06-2X 2.998_824734
M062X/6-311G*
E(RM062X) = -900.939646282

Zero-point correction= 0.158749 (Hartree/Particle)
Thermal correction to Energy= 0.174358
Thermal correction to Enthalpy= 0.175302
Thermal correction to Gibbs Free Energy= 0.114912
Sum of electronic and ZPE= -900.780897
Sum of electronic and thermal Energies= -900.765289
Sum of electronic and thermal Enthalpies= -900.764345
Sum of electronic and thermal Free Energies= -900.824734

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.411 54.607 127.100

C,0,-2.7949119261,0.1536749717,1.0268241998
C,0,-3.103787683,-0.6860289978,-0.0424756691
C,0,-2.1609325537,-1.5989240826,-0.5054846256
C,0,-0.8952631183,-1.6957306278,0.0849841299
C,0,-0.5979525781,-0.851783003,1.1561396532
C,0,-1.5370355233,0.0645596641,1.6254050006
C,0,0.1162133575,-2.6922976633,-0.4117102396
H,0,-3.5274286652,0.8629408147,1.3963824259
H,0,-4.0778697471,-0.6268238228,-0.515017582
H,0,-2.4067125156,-2.2445784846,-1.3433871982
H,0,0.3890964878,-0.8902796174,1.6013671663
H,0,-1.2840763898,0.7117779578,2.4588903124
H,0,-0.1580638181,-3.703142278,-0.09742468
H,0,1.1071623841,-2.4599771321,-0.0243534884
H,0,0.1691580598,-2.6825642427,-1.5013170065
N,0,-0.875738979,1.8239753323,-0.5586945233
O,0,-0.8306816105,1.016334854,-1.311003952
O,0,-0.9612110625,2.6928317951,0.1262817594
F,0,2.4800958657,-0.4871251044,0.6479258368
B,0,2.1349783676,0.4525129325,-0.3220206157
F,0,1.2406037281,1.4129713577,0.2625103519
F,0,3.2579339311,1.1189257885,-0.7913214368
F,0,1.4469829884,-0.1614684118,-1.3769258186

Pi Complex NO2BF4 PCM PURE-M06-2X 2.998_827902

M062X/6-311G*
E(RM062X) = -900.939593532

Zero-point correction= 0.157986 (Hartree/Particle)
Thermal correction to Energy= 0.173954
Thermal correction to Enthalpy= 0.174898
Thermal correction to Gibbs Free Energy= 0.111692
Sum of electronic and ZPE= -900.781607
Sum of electronic and thermal Energies= -900.765640
Sum of electronic and thermal Enthalpies= -900.764696
Sum of electronic and thermal Free Energies= -900.827902

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.158 54.795 133.029

C,0,2.3261664919,-0.9977053086,1.595017216
C,0,3.2444286429,-0.9812171634,0.5477972822
C,0,3.3383611639,0.1354955373,-0.2797369141
C,0,2.5215274204,1.2511216323,-0.0797911474
C,0,1.6020708209,1.2214150805,0.972339393
C,0,1.5028101612,0.1109205167,1.8038890261
C,0,2.6178076033,2.4625112585,-0.9686721955
H,0,2.2553526054,-1.8615532617,2.2471142446
H,0,3.8890580107,-1.8357819975,0.3762228813
H,0,4.054360979,0.1378907195,-1.0954277856
H,0,0.9421699659,2.067758007,1.129851912
H,0,0.7790137125,0.1090790979,2.6117751989
H,0,1.6339528491,2.7478549236,-1.3470613564
H,0,3.2734997056,2.2813034779,-1.8205549311
H,0,3.0133681192,3.3163913301,-0.4131905752
N,0,-0.0083644577,-1.408784007,-0.2398906701
O,0,0.5101320735,-0.8596762658,-1.0466101566
O,0,-0.4901324663,-2.0275108325,0.5413585726
F,0,-2.1396536164,-0.9131001387,-1.2177617466
B,0,-2.4221162664,0.3007403282,-0.5251559888
F,0,-3.5907160766,0.1692976578,0.1996976503
F,0,-1.3173041004,0.4849316226,0.3648222102
F,0,-2.4772033416,1.3518667853,-1.4207781197

Pi Complex NO2BF4 PCM PURE-M06-2X 3.031_827650
M062X/6-311G*
E(RM062X) = -900.940071851

Zero-point correction= 0.157810 (Hartree/Particle)
Thermal correction to Energy= 0.173753
Thermal correction to Enthalpy= 0.174697
Thermal correction to Gibbs Free Energy= 0.112422
Sum of electronic and ZPE= -900.782262
Sum of electronic and thermal Energies= -900.766319

Sum of electronic and thermal Enthalpies= -900.765374
Sum of electronic and thermal Free Energies= -900.827650

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.032 54.908 131.070

C,0,-1.2602447427,-4.2644566936,4.3445311373
C,0,0.1191807165,-4.1870584545,4.523436848
C,0,0.7612771242,-5.074495212,5.383866743
C,0,0.0430272411,-6.0505538488,6.0803148381
C,0,-1.3382901057,-6.1247289793,5.8853550899
C,0,-1.9870172963,-5.2419207269,5.0284396252
C,0,0.7167432509,-6.9818674506,7.0510727303
H,0,-1.7642891456,-3.5781452984,3.6729599356
H,0,0.6943315449,-3.4346729332,3.9956351038
H,0,1.8348305328,-5.0017532459,5.5259619178
H,0,-1.9152261683,-6.8602989991,6.4348765878
H,0,-3.062275814,-5.3067486749,4.9041828578
H,0,0.2928102195,-6.846765433,8.0485511612
H,0,1.7906700585,-6.7997248067,7.1006309119
H,0,0.5598646137,-8.0244813516,6.7654837687
N,0,-1.8015710136,-3.1174914837,7.0974977846
O,0,-0.8473563916,-3.5745655043,7.415856094
O,0,-2.7268973815,-2.5973530413,6.7801903458
F,0,-1.582820535,-5.5932034539,9.169302588
B,0,-2.7989487169,-4.9082323384,9.1356944755
F,0,-3.7140421043,-5.4280556553,10.0233173648
F,0,-2.5535970884,-3.5325372344,9.4018910111
F,0,-3.2969258983,-4.9523805803,7.80480338

Pi Complex NO2BF4 PCM PURE-M06-2X 3.038_828111
M062X/6-311G*
E(RM062X) = -900.940076145

Zero-point correction= 0.157750 (Hartree/Particle)
Thermal correction to Energy= 0.173744
Thermal correction to Enthalpy= 0.174688
Thermal correction to Gibbs Free Energy= 0.111965
Sum of electronic and ZPE= -900.782326
Sum of electronic and thermal Energies= -900.766333
Sum of electronic and thermal Enthalpies= -900.765388
Sum of electronic and thermal Free Energies= -900.828111

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.026 54.928 132.011

C,0,0.9372398306,-1.03456312,-0.5894022203

C,0,1.2386193959,-0.5680595086,-1.8671814269
C,0,2.3263766526,0.2798268293,-2.0610878496
C,0,3.1292015332,0.6791036651,-0.9887213449
C,0,2.821910539,0.1984052392,0.2863835501
C,0,1.7373716814,-0.6488841243,0.4884776871
C,0,4.2785626724,1.6315206933,-1.1771217036
H,0,0.0934189002,-1.6977808305,-0.4339637168
H,0,0.6260702873,-0.8630472931,-2.7117152237
H,0,2.549648742,0.6467208431,-3.0578513949
H,0,3.419012409,0.5165154876,1.133776086
H,0,1.5090606607,-0.9993225469,1.4890217622
H,0,4.3823494028,1.9320494463,-2.2201014568
H,0,5.2188042381,1.1758575639,-0.8582020999
H,0,4.1237955058,2.5255886979,-0.5692686741
N,0,-0.0953387157,1.6852248563,0.2871516647
O,0,0.6178703987,2.1245665953,-0.4333924838
O,0,-0.8610735707,1.2593413502,0.9650968432
F,0,0.2796806817,3.7088333327,1.6248722465
B,0,1.5207210005,3.2240783036,2.1237034977
F,0,2.5005542576,3.4202607564,1.1479973726
F,0,1.8450227578,3.8307627176,3.3159977647
F,0,1.3384787389,1.8251080455,2.2948551205

Pi Complex NO2BF4 PCM PURE-M06-2X 3.045_827735
M062X/6-311G*
E(RM062X) = -900.940077246

Zero-point correction= 0.157833 (Hartree/Particle)
Thermal correction to Energy= 0.173791
Thermal correction to Enthalpy= 0.174736
Thermal correction to Gibbs Free Energy= 0.112342
Sum of electronic and ZPE= -900.782244
Sum of electronic and thermal Energies= -900.766286
Sum of electronic and thermal Enthalpies= -900.765342
Sum of electronic and thermal Free Energies= -900.827735

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.056 54.909 131.318

C,0,2.9128898391,0.48379664,-0.5840324522
C,0,3.2071640834,-0.2621321151,0.5554947614
C,0,2.4593050375,-1.3974112637,0.8575998013
C,0,1.4071365515,-1.8078687061,0.0338873318
C,0,1.1267354132,-1.0563591505,-1.109703145
C,0,1.8686414884,0.0792132746,-1.4183339631
C,0,0.5633347991,-3.0064141792,0.3730157476
H,0,3.4955910893,1.3659459221,-0.8256164973
H,0,4.0173584262,0.0413043151,1.2089204388
H,0,2.6880378552,-1.9685095168,1.7517430709

H,0,0.2975911774,-1.3442809923,-1.7464203674
H,0,1.6259649551,0.6544530341,-2.3050354586
H,0,-0.4805097987,-2.7068034287,0.4884465879
H,0,0.8947819039,-3.4808562736,1.2971254829
H,0,0.604886307,-3.7501548982,-0.4260829307
N,0,0.3636959215,1.5944459669,0.6560394545
O,0,0.3102315514,0.6530444936,1.2319263813
O,0,0.4408169271,2.5691131708,0.1349877371
F,0,-1.9421347651,-0.6496399056,0.2378920759
B,0,-2.172463991,0.6113776041,-0.3144720273
F,0,-1.1022100971,0.9097232923,-1.2009200654
F,0,-3.3851389809,0.6837206155,-0.9612487511
F,0,-2.0870646935,1.5843261004,0.7216187863

Pi Complex NO2BF4 PCM PURE-M06-2X 3.082_828846
M062X/6-311G*
E(RM062X) = -900.938785019

Zero-point correction= 0.157858 (Hartree/Particle)
Thermal correction to Energy= 0.174061
Thermal correction to Enthalpy= 0.175005
Thermal correction to Gibbs Free Energy= 0.109939
Sum of electronic and ZPE= -900.780927
Sum of electronic and thermal Energies= -900.764724
Sum of electronic and thermal Enthalpies= -900.763780
Sum of electronic and thermal Free Energies= -900.828846

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.225 54.856 136.942

C,0,1.3409027005,1.552797146,-1.0520858244
C,0,1.8091977332,1.8374741283,0.2295760222
C,0,2.8357901158,1.0803245579,0.7819690563
C,0,3.412892438,0.0192900195,0.0754096601
C,0,2.9332802289,-0.2600284394,-1.2060279567
C,0,1.9100167637,0.5036472433,-1.7696123857
C,0,4.5364265117,-0.7787426359,0.6816968552
H,0,0.5312544001,2.13161121,-1.4781459947
H,0,1.3666046753,2.6460735721,0.7998590625
H,0,3.1934108277,1.3078709992,1.7813684323
H,0,3.3662127218,-1.0781001374,-1.7733688517
H,0,1.5560081803,0.2753658958,-2.7696536449
H,0,4.3370093971,-1.0079116499,1.7300353251
H,0,5.4707146091,-0.2124937846,0.6440528147
H,0,4.6936130858,-1.7163336121,0.1479092798
N,0,-0.0321601093,-1.0903428283,-0.2612124699
O,0,0.4278772044,-0.8565045538,0.7158620969
O,0,-0.4350034912,-1.383175228,-1.2490525605
F,0,-2.1671837211,-1.2972614172,0.7470229202

B,0,-2.6391990552,0.0413360766,0.586338501
F,0,-1.5900287795,0.7329468481,-0.0972198282
F,0,-3.7839862318,0.0421990504,-0.1884343734
F,0,-2.8433322049,0.6173545392,1.8262228637

Pi Complex NO2BF4 PCM PURE-M06-2X 3.181_825313
M062X/6-311G*
E(RM062X) = -900.939838216

Zero-point correction= 0.158489 (Hartree/Particle)
Thermal correction to Energy= 0.174100
Thermal correction to Enthalpy= 0.175044
Thermal correction to Gibbs Free Energy= 0.114525
Sum of electronic and ZPE= -900.781349
Sum of electronic and thermal Energies= -900.765738
Sum of electronic and thermal Enthalpies= -900.764794
Sum of electronic and thermal Free Energies= -900.825313

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.249 54.580 127.373

C,0,0.4280663924,-1.7326195446,-0.5014703286
C,0,-0.8768651758,-1.4904098778,-0.9386734265
C,0,-1.1829461102,-0.315576944,-1.6198432413
C,0,-0.1986183173,0.6452802881,-1.8712634458
C,0,1.1024849863,0.3906863156,-1.4339126823
C,0,1.4169129862,-0.7881233592,-0.7567074546
C,0,-0.5723088549,1.9248464361,-2.5682857944
H,0,0.6668482746,-2.6491723107,0.0256992781
H,0,-1.6610252878,-2.2163578079,-0.7496778096
H,0,-2.1991929879,-0.1309933478,-1.947410824
H,0,1.8802270878,1.1256013759,-1.6174440685
H,0,2.4344116711,-0.9641845782,-0.4259745228
H,0,-1.373606563,2.4228435778,-2.0193229524
H,0,-0.9507381629,1.7221328071,-3.5730983238
H,0,0.278383947,2.6016264599,-2.6528410799
N,0,-1.2248234453,0.2343076169,1.3737717494
O,0,-0.340178919,0.8650553916,1.1622240997
O,0,-2.0712799838,-0.4107536811,1.6788385917
F,0,-2.543628696,1.7438204997,0.2304453368
B,0,-3.7932030496,1.3180654787,-0.3385998047
F,0,-4.8269080586,1.978211481,0.3060972398
F,0,-3.778657898,1.6026297152,-1.7002811201
F,0,-3.8836951352,-0.0684010923,-0.129921616

Pi Complex NO2BF4 PCM PURE-M06-2X 3.187_824934
M062X/6-311G*
E(RM062X) = -900.939888477

Zero-point correction= 0.158650 (Hartree/Particle)
Thermal correction to Energy= 0.174211
Thermal correction to Enthalpy= 0.175155
Thermal correction to Gibbs Free Energy= 0.114954
Sum of electronic and ZPE= -900.781239
Sum of electronic and thermal Energies= -900.765678
Sum of electronic and thermal Enthalpies= -900.764734
Sum of electronic and thermal Free Energies= -900.824934

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.319 54.545 126.703

C,0,2.7045212267,-0.1849626679,1.3212967143
C,0,3.2452063549,0.6317890523,0.3322788173
C,0,2.4370823851,1.551051905,-0.3349009785
C,0,1.0804629258,1.6773795667,-0.025004564
C,0,0.5501062507,0.8621069867,0.9779499425
C,0,1.3509756663,-0.0644010797,1.6427658722
C,0,0.1916809936,2.6552706487,-0.7448846336
H,0,3.3277888973,-0.904431011,1.839938336
H,0,4.294870174,0.5487346277,0.0734719138
H,0,2.8649497372,2.1727243806,-1.1155409891
H,0,-0.5025969604,0.9401679062,1.2229437791
H,0,0.9134970938,-0.6938475181,2.4108958226
H,0,0.562643117,2.8669841738,-1.7488461973
H,0,0.1428212655,3.6032470084,-0.2018296658
H,0,-0.8212801653,2.258325724,-0.8173257953
N,0,0.7294055613,-1.6788101951,-0.685250406
O,0,0.2201213226,-2.4027040557,-0.0203042457
O,0,1.2915579471,-1.0344423303,-1.3882901476
F,0,-3.3642110674,-1.1348018418,-0.775157018
B,0,-2.2770046382,-0.4758894384,-0.2245416541
F,0,-1.8250565007,-1.1400175776,0.9276679577
F,0,-1.1939042721,-0.4944690216,-1.167793754
F,0,-2.5838313147,0.8494277575,0.0719598935

Pi Complex NO2BF4 PCM PURE-M06-2X 3.188_825412
M062X/6-311G*
E(RM062X) = -900.939815265

Zero-point correction= 0.158459 (Hartree/Particle)
Thermal correction to Energy= 0.174067
Thermal correction to Enthalpy= 0.175011
Thermal correction to Gibbs Free Energy= 0.114403
Sum of electronic and ZPE= -900.781356
Sum of electronic and thermal Energies= -900.765748
Sum of electronic and thermal Enthalpies= -900.764804
Sum of electronic and thermal Free Energies= -900.825412

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.229 54.568 127.561

C,0,-1.7898816071,-2.8902163023,-1.0844161286
C,0,-0.5995805204,-2.175573497,-1.0008772486
C,0,0.3456603445,-2.4998846375,-0.0269771826
C,0,0.1239174738,-3.5427106509,0.8740693341
C,0,-1.0707997664,-4.2629554471,0.7743780492
C,0,-2.0209992221,-3.9390190393,-0.1903220578
C,0,1.1117366064,-3.8850741552,1.9553850373
H,0,-2.5270012112,-2.6427349893,-1.839626743
H,0,-0.4048927542,-1.3612716155,-1.6898852617
H,0,1.2662635954,-1.9278653365,0.035549755
H,0,-1.2601737197,-5.0738742757,1.4679582795
H,0,-2.9427673681,-4.5091755559,-0.2439585396
H,0,0.6284618307,-3.8150230492,2.931443982
H,0,1.9764373761,-3.2210565072,1.9355367197
H,0,1.4654362899,-4.9131143963,1.8466786042
N,0,-2.7682530898,-1.947087017,1.7995704401
O,0,-1.8369482361,-1.3573833986,1.6975253889
O,0,-3.7504543013,-2.4507005432,1.885226629
F,0,-1.8118020739,-3.1130210107,3.5460317168
B,0,-2.2880495354,-4.4264073837,3.8834456185
F,0,-1.2183800543,-5.3137667293,3.8246162866
F,0,-2.8468509034,-4.3887171258,5.1501803492
F,0,-3.2568256535,-4.7666943367,2.9235255716

Pi Complex NO2BF4 PCM PURE-M06-2X 3.189_824858
M062X/6-311G*
E(RM062X) = -900.939899573

Zero-point correction= 0.158697 (Hartree/Particle)
Thermal correction to Energy= 0.174251
Thermal correction to Enthalpy= 0.175195
Thermal correction to Gibbs Free Energy= 0.115042
Sum of electronic and ZPE= -900.781203
Sum of electronic and thermal Energies= -900.765649
Sum of electronic and thermal Enthalpies= -900.764704
Sum of electronic and thermal Free Energies= -900.824858

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.344 54.522 126.603

C,0,2.906949854,0.6761250119,0.6403598081
C,0,1.7026454713,0.4796855419,1.3194966808
C,0,0.8962586933,-0.6158625268,1.0185719656
C,0,1.2700919418,-1.5306947325,0.0306329341
C,0,2.4786470157,-1.3259171773,-0.6397507529

C,0,3.2930522267,-0.2351602865,-0.3384158064
C,0,0.374100766,-2.6965291438,-0.2894638802
H,0,3.5358723271,1.526749423,0.876832242
H,0,1.3869269029,1.1801544495,2.0858086727
H,0,-0.0428142126,-0.7536492233,1.5412832925
H,0,2.782727701,-2.0230945521,-1.4146394746
H,0,4.2256047884,-0.0946966779,-0.8735443063
H,0,0.5759408892,-3.5329238694,0.385620335
H,0,0.5281163425,-3.0494938184,-1.3101824577
H,0,-0.6712632255,-2.4122765814,-0.165273172
N,0,0.3280920719,1.6097963877,-0.9859398642
O,0,0.7785837929,0.9095046679,-1.715248253
O,0,-0.0897374992,2.3854794416,-0.3156547103
F,0,-1.6643419159,1.1209860658,1.2996211953
B,0,-2.2873367769,0.2286169927,0.4119907963
F,0,-2.3231970044,-1.0514091359,0.9600225204
F,0,-3.557585808,0.6720884578,0.0817930856
F,0,-1.4819583423,0.1928472853,-0.7770988508

Pi Complex NO2BF4 PCM PURE-M06-2X 3.189_825651
M062X/6-311G*
E(RM062X) = -900.939827037

Zero-point correction= 0.158396 (Hartree/Particle)
Thermal correction to Energy= 0.174055
Thermal correction to Enthalpy= 0.175000
Thermal correction to Gibbs Free Energy= 0.114176
Sum of electronic and ZPE= -900.781431
Sum of electronic and thermal Energies= -900.765772
Sum of electronic and thermal Enthalpies= -900.764827
Sum of electronic and thermal Free Energies= -900.825651

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.221 54.598 128.015

C,0,-2.8322277737,-4.3493292628,-0.5116668038
C,0,-3.667235587,-4.1647892802,-1.608547912
C,0,-3.1498717338,-3.6768793048,-2.8091685598
C,0,-1.7942871648,-3.3700547127,-2.9379935606
C,0,-0.9608515209,-3.5695585454,-1.8326524329
C,0,-1.4725605128,-4.0494064043,-0.6301492958
C,0,-1.2200944782,-2.808793641,-4.2100228555
H,0,-3.2293098322,-4.7282120382,0.4230635203
H,0,-4.7238371009,-4.3958827201,-1.5320010745
H,0,-3.813341374,-3.5266122589,-3.6552643303
H,0,0.0932326566,-3.3321167277,-1.9143343704
H,0,-0.8065905302,-4.1902796844,0.2149749152
H,0,-0.468522359,-3.483813184,-4.6266906285
H,0,-0.7193007142,-1.8618319623,-4.0017449387

H,0,-1.9913164518,-2.648443811,-4.9639829312
N,0,-2.1493765293,-1.2432430388,-0.2697897675
O,0,-1.4674550503,-1.2249394669,0.6020611972
O,0,-2.9023659254,-1.2237631015,-1.0809568547
F,0,1.360184381,-1.4565717658,-2.6151181554
B,0,0.8405232884,-0.7731135942,-1.5200359247
F,0,0.9062529773,-1.5740107098,-0.3681894755
F,0,1.4951244501,0.4310238132,-1.3178006871
F,0,-0.5516799148,-0.5098549984,-1.7650949737

Pi Complex NO2BF4 PCM PURE-M06-2X 3.234_824226
M062X/6-311G*
E(RM062X) = -900.936710619

Zero-point correction= 0.158182 (Hartree/Particle)
Thermal correction to Energy= 0.174185
Thermal correction to Enthalpy= 0.175130
Thermal correction to Gibbs Free Energy= 0.112484
Sum of electronic and ZPE= -900.778528
Sum of electronic and thermal Energies= -900.762525
Sum of electronic and thermal Enthalpies= -900.761581
Sum of electronic and thermal Free Energies= -900.824226

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.303 54.812 131.849

C,0,4.2454573101,-2.7180703235,-0.4866097869
C,0,4.350940463,-2.4569922,-1.8510129158
C,0,4.8477056999,-1.2364458466,-2.2970307528
C,0,5.2473744787,-0.2457346836,-1.3931916373
C,0,5.1336632167,-0.5153280291,-0.0280829248
C,0,4.6401325675,-1.7435286787,0.4235388461
C,0,5.7986406315,1.0660014965,-1.8883174114
H,0,3.8283549103,-3.6550953067,-0.1402010726
H,0,4.0258104032,-3.2024701189,-2.5672687481
H,0,4.9203473608,-1.0423806986,-3.3629625656
H,0,5.4423623343,0.2368249608,0.6920520287
H,0,4.5573182908,-1.9326088384,1.4886130777
H,0,6.7802341379,0.9214172881,-2.3461284374
H,0,5.9120200447,1.7826212543,-1.0741052179
H,0,5.1487012093,1.5073752087,-2.6467328101
N,0,2.1751754636,-0.2799855106,-0.0061144746
O,0,2.1156760675,-0.5746967332,-1.069072002
O,0,2.1949311974,0.105385034,1.0340969724
F,0,1.6935304338,-4.5235858425,0.2539199869
B,0,0.9802209843,-3.3697625154,-0.0572402315
F,0,1.2304063877,-2.9757363945,-1.3790082068
F,0,-0.3801442817,-3.5504583581,0.150160195
F,0,1.4344069886,-2.3036571639,0.7939556888

Pi Complex NO2BF4 PCM PURE-M06-2X 3.278_828463
M062X/6-311G*
E(RM062X) = -900.941417319

Zero-point correction= 0.158272 (Hartree/Particle)
Thermal correction to Energy= 0.174123
Thermal correction to Enthalpy= 0.175068
Thermal correction to Gibbs Free Energy= 0.112955
Sum of electronic and ZPE= -900.783145
Sum of electronic and thermal Energies= -900.767294
Sum of electronic and thermal Enthalpies= -900.766350
Sum of electronic and thermal Free Energies= -900.828463

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.264 54.696 130.727

C,0,-1.1872823781,3.6315802963,0.8289433573
C,0,-1.6006933305,2.3358517309,1.1447693826
C,0,-0.6646129431,1.3129218045,1.2739732178
C,0,0.7008511922,1.5597493949,1.0922390447
C,0,1.1000279451,2.8617355832,0.7864226113
C,0,0.1676172991,3.8904714185,0.6532380911
C,0,1.6961892241,0.4364596811,1.1998545557
H,0,-1.9152522665,4.4286399419,0.7317288147
H,0,-2.6539625483,2.1249669462,1.2980413875
H,0,-0.9939258097,0.3057988156,1.5076985684
H,0,2.1545415802,3.0743897777,0.6423730293
H,0,0.5018077912,4.8929753016,0.4108045462
H,0,1.6058574083,-0.0723972405,2.1622800976
H,0,2.7190600725,0.8007326873,1.1015654659
H,0,1.5115000003,-0.3033614011,0.4180668548
N,0,-1.2826613721,1.5472679034,-1.6995791587
O,0,-2.3131839366,1.1443925852,-1.6707217138
O,0,-0.2846470534,2.017251015,-1.7596166233
F,0,-0.5543961358,-0.1634651169,-3.2286461017
B,0,-0.0534207317,-1.095951756,-2.2750697654
F,0,-0.4290811778,-0.5590085834,-1.0028610684
F,0,-0.6423373646,-2.3303996711,-2.4584461281
F,0,1.3267164353,-1.1571044144,-2.3525722657

Pi Complex NO2BF4 PCM PURE-M06-2X 3.281_828248
M062X/6-311G*
E(RM062X) = -900.941709578

Zero-point correction= 0.158256 (Hartree/Particle)
Thermal correction to Energy= 0.173992
Thermal correction to Enthalpy= 0.174936
Thermal correction to Gibbs Free Energy= 0.113462

Sum of electronic and ZPE= -900.783454
Sum of electronic and thermal Energies= -900.767718
Sum of electronic and thermal Enthalpies= -900.766774
Sum of electronic and thermal Free Energies= -900.828248

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.182 54.666 129.384

C,0,-0.3566508889,0.2877816534,3.2797219507
C,0,-1.017303971,1.3231369554,2.6172649763
C,0,-1.5667873415,1.1106021483,1.3547470394
C,0,-1.4664735306,-0.1346730182,0.7269279174
C,0,-0.8169817951,-1.1663138205,1.4086650706
C,0,-0.2639025471,-0.9602889129,2.671484038
C,0,-1.9934855423,-0.3343767733,-0.6679978928
H,0,0.0676522092,0.4517344852,4.2634818719
H,0,-1.1110486499,2.2961182632,3.0884265651
H,0,-2.0681344428,1.9238314407,0.8412216525
H,0,-0.7356536326,-2.1429671768,0.9418357425
H,0,0.2396478452,-1.7752132232,3.1792195977
H,0,-2.2342050084,-1.381459989,-0.8561158875
H,0,-1.2436935346,-0.0164637601,-1.397314509
H,0,-2.8890166106,0.2645419352,-0.8403278015
N,0,1.3752701838,1.7409685849,0.9023599153
O,0,1.3491740029,2.8121030462,1.1811729391
O,0,1.4561031021,0.6611383587,0.6832932984
F,0,-0.0757077989,2.1633850917,-0.9387803872
B,0,0.8923215701,2.1969346228,-1.9919230208
F,0,0.723382196,3.3343317993,-2.7551557187
F,0,2.153984686,2.2248122687,-1.3293813725
F,0,0.7822085992,1.0381631201,-2.744592885

Pi Complex NO2BF4 PCM PURE-M06-2X 3.293_826543
M062X/6-311G*
E(RM062X) = -900.938018478

Zero-point correction= 0.157623 (Hartree/Particle)
Thermal correction to Energy= 0.173649
Thermal correction to Enthalpy= 0.174593
Thermal correction to Gibbs Free Energy= 0.111476
Sum of electronic and ZPE= -900.780396
Sum of electronic and thermal Energies= -900.764369
Sum of electronic and thermal Enthalpies= -900.763425
Sum of electronic and thermal Free Energies= -900.826543

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.966 54.877 132.842

C,0,-0.1282562982,-0.4948018958,4.1134327163
C,0,-0.2961572025,0.8846727328,4.0708531952
C,0,-1.5759675064,1.4382677229,4.0439683119
C,0,-2.7113003767,0.6272981097,4.0656482516
C,0,-2.5301524166,-0.7601887345,4.1125490878
C,0,-1.2519434244,-1.319208929,4.1364489789
C,0,-4.0946098501,1.2233621543,4.0696873062
H,0,0.8577187468,-0.9408960104,4.1012599901
H,0,0.5701917111,1.5362262784,4.0468962433
H,0,-1.6938814737,2.5165620313,4.0024138837
H,0,-3.4008906631,-1.4100955893,4.1377410211
H,0,-1.1280662067,-2.3955884728,4.1602352611
H,0,-4.0814796559,2.257268563,3.7228448625
H,0,-4.5113524577,1.2169647623,5.0801886737
H,0,-4.7760296997,0.6554060978,3.4335586669
N,0,-1.7525657384,-1.0170713715,1.2969635208
O,0,-2.2974158455,-1.9783353499,1.2297385898
O,0,-1.2726551872,-0.0195145598,1.287124108
F,0,-0.7875700467,-3.8557367788,2.1938555591
B,0,0.4944007611,-3.3134807342,2.0098285304
F,0,0.316800947,-2.0152952771,1.4195050296
F,0,1.1311253983,-3.1615932612,3.2383985913
F,0,1.243960185,-4.0982222882,1.1483676204

Pi Complex NO2BF4 PCM PURE-M06-2X 3.351_828876
M062X/6-311G*
E(RM062X) = -900.941679148

Zero-point correction= 0.158260 (Hartree/Particle)
Thermal correction to Energy= 0.174035
Thermal correction to Enthalpy= 0.174979
Thermal correction to Gibbs Free Energy= 0.112803
Sum of electronic and ZPE= -900.783419
Sum of electronic and thermal Energies= -900.767644
Sum of electronic and thermal Enthalpies= -900.766700
Sum of electronic and thermal Free Energies= -900.828876

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.208 54.679 130.861

C,0,-4.6720445495,-1.3561255034,0.0203870703
C,0,-4.0514805331,-0.9090785365,1.1856874949
C,0,-3.4466628142,0.348286831,1.2226614287
C,0,-3.4514351224,1.181294076,0.100604797
C,0,-4.0859034092,0.7224786301,-1.0574047248
C,0,-4.6893521908,-0.531051507,-1.1019237694
C,0,-2.762728993,2.5184614793,0.1098115952
H,0,-5.1454877372,-2.330613761,-0.0082514475
H,0,-4.0455125429,-1.5353432653,2.0717808001

H,0,-2.9605912596,0.6852607227,2.1325295772
H,0,-4.0987138151,1.3560014876,-1.9391606113
H,0,-5.1720449687,-0.864744547,-2.0135509607
H,0,-2.4899957302,2.8162328407,1.1220968222
H,0,-3.4029990503,3.2900238791,-0.3225837646
H,0,-1.8436234147,2.4677286801,-0.4779655286
N,0,-1.3218533119,-1.4187658636,0.069717911
O,0,-1.6459235674,-1.0374954521,-0.9156162625
O,0,-1.011872907,-1.8714129426,1.0309213704
F,0,0.2298573296,1.3796541435,-1.262637894
B,0,0.6373850368,0.7304334351,-0.1027873223
F,0,1.7248675624,1.3379779894,0.4833770313
F,0,-0.4649056507,0.6897131985,0.8035124478
F,0,0.9197456392,-0.6307580148,-0.4058130602

Pi Complex NO2BF4 PCM PURE-M06-2X 3.378_823817
M062X/6-311G*
E(RM062X) = -900.938779720

Zero-point correction= 0.158695 (Hartree/Particle)
Thermal correction to Energy= 0.174204
Thermal correction to Enthalpy= 0.175148
Thermal correction to Gibbs Free Energy= 0.114963
Sum of electronic and ZPE= -900.780085
Sum of electronic and thermal Energies= -900.764576
Sum of electronic and thermal Enthalpies= -900.763632
Sum of electronic and thermal Free Energies= -900.823817

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.315 54.548 126.670

C,0,-3.1766916697,0.405147725,-0.789498797
C,0,-2.037032545,0.3016477909,-1.5828908326
C,0,-1.0334735513,-0.6134374831,-1.2559575198
C,0,-1.1526020698,-1.4438623184,-0.1380408884
C,0,-2.2995758103,-1.3239059835,0.651823331
C,0,-3.3013630857,-0.4106118491,0.3331253321
C,0,-0.0873868727,-2.4541416438,0.1907296624
H,0,-3.9580387174,1.1122639684,-1.0427481569
H,0,-1.9279694011,0.9270131031,-2.4627620672
H,0,-0.1396293818,-0.6785748587,-1.8660883709
H,0,-2.4075644588,-1.9533989559,1.529878419
H,0,-4.1809483348,-0.3349826503,0.9627124025
H,0,0.1617213647,-2.4267892054,1.2521329649
H,0,0.8229710252,-2.2558962635,-0.3736149469
H,0,-0.4338908879,-3.4628099088,-0.049882836
N,0,-0.268253384,1.6874279109,0.3533189997
O,0,0.4268644823,2.023661483,-0.440905313
O,0,-0.9902187976,1.4521221152,1.1580293576

F,0,2.9879599237,1.2656209989,0.4947580692
B,0,2.3759347562,0.0179948248,0.3726966965
F,0,1.1556426582,0.0680538817,1.1316819179
F,0,2.0235910136,-0.2008502546,-0.967384807
F,0,3.172539744,-1.0024554269,0.853802383

Pi Complex NO2BF4 PCM PURE-M06-2X 3.379_825489
M062X/6-311G*
E(RM062X) = -900.938705281

Zero-point correction= 0.158235 (Hartree/Particle)
Thermal correction to Energy= 0.174004
Thermal correction to Enthalpy= 0.174948
Thermal correction to Gibbs Free Energy= 0.113216
Sum of electronic and ZPE= -900.780471
Sum of electronic and thermal Energies= -900.764702
Sum of electronic and thermal Enthalpies= -900.763758
Sum of electronic and thermal Free Energies= -900.825489

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.189 54.728 129.925

C,0,5.0359678023,-1.4192549029,-3.5178172376
C,0,5.5163269546,-0.2064617963,-3.0278772333
C,0,5.5411052512,0.0361996888,-1.6568274354
C,0,5.0883048008,-0.9212340681,-0.7444408747
C,0,4.6012885266,-2.1307734932,-1.2476470599
C,0,4.577052603,-2.3811579742,-2.6218724752
C,0,5.1434704099,-0.6668656478,0.7372949252
H,0,5.0207182965,-1.6123130039,-4.5841944042
H,0,5.8715229629,0.5530858533,-3.7154297582
H,0,5.9158313423,0.9858671958,-1.28717423
H,0,4.2296909006,-2.8775160651,-0.5551966665
H,0,4.2061641078,-3.332748548,-2.9879000488
H,0,4.5538543304,-1.4036484643,1.2814570403
H,0,4.7472508438,0.3201254518,0.9779599772
H,0,6.1763110135,-0.714116059,1.0925764109
N,0,2.0563904881,-0.9317489485,-1.9997373851
O,0,2.5276604311,0.0016387013,-2.3613136262
O,0,1.5191447449,-1.8599274986,-1.7219372119
F,0,2.2716177534,-0.2303421659,0.1656389745
B,0,1.7570064829,-1.168919609,1.1268052571
F,0,2.3420830975,-2.4135627568,0.8448695467
F,0,2.0835065409,-0.7409487248,2.3995503658
F,0,0.379534815,-1.2473267648,0.9347260495

Pi Complex NO2BF4 PCM PURE-M06-2X 3.423_822985
M062X/6-311G*
E(RM062X) = -900.937556839

Zero-point correction= 0.158613 (Hartree/Particle)
Thermal correction to Energy= 0.174294
Thermal correction to Enthalpy= 0.175238
Thermal correction to Gibbs Free Energy= 0.114572
Sum of electronic and ZPE= -900.778944
Sum of electronic and thermal Energies= -900.763263
Sum of electronic and thermal Enthalpies= -900.762319
Sum of electronic and thermal Free Energies= -900.822985

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.371 54.626 127.683

C,0,0.4017946698,1.7110812507,0.3101736678
C,0,0.7281748427,0.7384032063,1.2502803114
C,0,1.9392528611,0.0551391118,1.15327642
C,0,2.844298533,0.3261514132,0.1184166259
C,0,2.502551002,1.3056606558,-0.8157280724
C,0,1.2949781459,1.9958026259,-0.7185245211
C,0,4.1617192961,-0.4007610354,0.0489542608
H,0,-0.557111968,2.2076028088,0.3666955866
H,0,0.0232963472,0.4946436756,2.0353369808
H,0,2.1897457521,-0.7022884386,1.8911795012
H,0,3.1877327573,1.5313803101,-1.6268665492
H,0,1.0458934397,2.7478851161,-1.4587308992
H,0,4.0552763778,-1.4458651468,0.3467256759
H,0,4.8868955108,0.0568906014,0.7269327344
H,0,4.582582051,-0.3702735109,-0.9567134437
N,0,0.4197669688,-1.5536495995,-0.7186796746
O,0,0.2071828859,-0.7291272943,-1.4222657297
O,0,0.6627458674,-2.4365707849,-0.0920823649
F,0,-2.3722881807,0.7533954637,1.286801276
B,0,-2.4414282147,-0.1864708741,0.2612929516
F,0,-2.0892801726,0.3946523026,-0.9643214095
F,0,-1.483566439,-1.2262722208,0.5270401398
F,0,-3.7037773337,-0.7562396369,0.1897185318

Pi Complex NO2BF4 PCM PURE-M06-2X 3.534_823904
M062X/6-311G*
E(RM062X) = -900.937909738

Zero-point correction= 0.158688 (Hartree/Particle)
Thermal correction to Energy= 0.174418
Thermal correction to Enthalpy= 0.175362
Thermal correction to Gibbs Free Energy= 0.114005
Sum of electronic and ZPE= -900.779222
Sum of electronic and thermal Energies= -900.763492
Sum of electronic and thermal Enthalpies= -900.762548
Sum of electronic and thermal Free Energies= -900.823904

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.449 54.572 129.136

C,0,-0.1827941978,0.2710149976,4.1029893471
C,0,-0.5586636205,1.4778532671,3.5152248257
C,0,-1.7991906838,1.601067815,2.895548805
C,0,-2.6890395883,0.5243948776,2.8554795715
C,0,-2.2942166155,-0.6851518431,3.4422925836
C,0,-1.0528442145,-0.8143756347,4.0630405722
C,0,-4.0532673079,0.6682286928,2.2327242557
H,0,0.7870320144,0.174580425,4.5768642047
H,0,0.1177476268,2.325082974,3.5359859398
H,0,-2.0835087382,2.5448127762,2.4408573187
H,0,-2.9583561717,-1.5426129381,3.4066769306
H,0,-0.7653888027,-1.7675403734,4.4903206773
H,0,-4.7902878347,0.93437274,2.9949556785
H,0,-4.3861171335,-0.2648821686,1.7741758964
H,0,-4.0657504871,1.451787923,1.4739016776
N,0,-0.9710671392,-1.1700906807,0.9739511364
O,0,-1.7980523853,-1.8489011527,0.6863754483
O,0,-0.1434470013,-0.456901479,1.1533270096
F,0,-1.8354157599,-3.6100469986,2.6341818651
B,0,-0.4611318306,-3.8927924241,2.7176449467
F,0,0.2237135286,-2.8168810341,2.0593462666
F,0,-0.0561607853,-3.9328434937,4.0482510546
F,0,-0.1666673721,-5.0787564677,2.0633665884
Pi Complex NO2BF4 PCM PURE-M06-2X 3.645_825367
M062X/6-311G*
E(RM062X) = -900.939301383

Zero-point correction= 0.158242 (Hartree/Particle)
Thermal correction to Energy= 0.174002
Thermal correction to Enthalpy= 0.174946
Thermal correction to Gibbs Free Energy= 0.113935
Sum of electronic and ZPE= -900.781059
Sum of electronic and thermal Energies= -900.765299
Sum of electronic and thermal Enthalpies= -900.764355
Sum of electronic and thermal Free Energies= -900.825367

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.188 54.800 128.409

C,0,-3.3774283996,-0.5490399188,0.7441193801
C,0,-2.4252231216,0.1666412721,1.4692105575
C,0,-1.5037190101,0.9743913772,0.8131193981
C,0,-1.5207855639,1.0880298281,-0.5825299331
C,0,-2.4796030763,0.361043599,-1.3001722189

C,0,-3.4026111038,-0.4504206569,-0.6440070119
C,0,-0.5421555025,1.9921391313,-1.2852106194
H,0,-4.0906115952,-1.1828845432,1.2583036371
H,0,-2.394347408,0.0853075844,2.549742893
H,0,-0.7437674509,1.5047551527,1.3751760737
H,0,-2.506176698,0.4410404415,-2.3829315661
H,0,-4.1376131209,-1.0036604171,-1.2174029247
H,0,-0.8661500535,3.0325949134,-1.1962779136
H,0,-0.4749433335,1.7601298805,-2.3497924395
H,0,0.4530968102,1.9228107284,-0.843724195
N,0,-0.1593801647,-1.4104047382,-0.7358147305
O,0,-0.7885982834,-1.9690477065,-0.0154037438
O,0,0.4839737901,-0.9527153849,-1.5140411295
F,0,2.3709172822,0.5031175326,-0.5214230599
B,0,2.1019300588,0.4198355529,0.8535514224
F,0,3.2363193042,0.0578088338,1.5598633814
F,0,1.5856287256,1.6316580191,1.3112346512
F,0,1.0993409148,-0.5941524813,1.0214040911

Pi Complex NO2BF4 PCM PURE-M06-2X 3.689_828697
M062X/6-311G*
E(RM062X) = -900.940818005

Zero-point correction= 0.157931 (Hartree/Particle)
Thermal correction to Energy= 0.173884
Thermal correction to Enthalpy= 0.174828
Thermal correction to Gibbs Free Energy= 0.112121
Sum of electronic and ZPE= -900.782887
Sum of electronic and thermal Energies= -900.766934
Sum of electronic and thermal Enthalpies= -900.765990
Sum of electronic and thermal Free Energies= -900.828697

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.114 54.838 131.980

C,0,3.5239603318,-3.107381134,0.3385598937
C,0,3.9653116205,-1.9103904588,0.9035781095
C,0,3.9904230906,-1.7551489644,2.2834862183
C,0,3.5762385835,-2.7907196001,3.1301626937
C,0,3.1382031206,-3.9866461465,2.551613153
C,0,3.1114029379,-4.1461733514,1.1657555847
C,0,3.6135523984,-2.6070914127,4.6245992043
H,0,3.4990691624,-3.2247822722,-0.7385062341
H,0,4.2803130404,-1.0939786016,0.2637427592
H,0,4.3123727018,-0.8146983167,2.7171257173
H,0,2.8202134519,-4.8031985046,3.193394659
H,0,2.7677821861,-5.081041323,0.7377470512
H,0,4.6455987948,-2.5988104861,4.9834653318
H,0,3.089221161,-3.4122316009,5.1418438574

H,0,3.1596681271,-1.6553553988,4.9068638133
N,0,0.7704594187,-2.1939564854,2.617102198
O,0,0.9766599879,-1.8876404998,1.5750730053
O,0,0.507085039,-2.5530689592,3.6311810888
F,0,1.0617540931,1.2201335107,1.918341358
B,0,0.6847463688,0.6790951457,3.1373414844
F,0,0.4429634538,1.6421793567,4.0918148578
F,0,-0.4617262884,-0.1438631009,2.9505512321
F,0,1.7135333182,-0.2128960959,3.580349163

Pi Complex NO2BF4 PCM PURE-M06-2X 3.732_828669
M062X/6-311G*
E(RM062X) = -900.941337422

Zero-point correction= 0.158135 (Hartree/Particle)
Thermal correction to Energy= 0.174048
Thermal correction to Enthalpy= 0.174992
Thermal correction to Gibbs Free Energy= 0.112668
Sum of electronic and ZPE= -900.783203
Sum of electronic and thermal Energies= -900.767290
Sum of electronic and thermal Enthalpies= -900.766345
Sum of electronic and thermal Free Energies= -900.828669

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.217 54.811 131.171

C,0,2.0296250026,3.3580986294,-0.9172365859
C,0,1.3634673117,3.2950016454,0.3020153471
C,0,1.6977269818,2.307794741,1.2291035816
C,0,2.6985276153,1.369627402,0.9523369127
C,0,3.3596808587,1.4471545694,-0.2789321807
C,0,3.03208978,2.4313120286,-1.2032250613
C,0,3.0705337203,0.3008328745,1.9467914117
H,0,1.7696024559,4.1211825851,-1.6416558061
H,0,0.5836269764,4.0113305191,0.5344648761
H,0,1.1774949453,2.2662640506,2.1817766363
H,0,4.1234821196,0.7141887153,-0.5149429536
H,0,3.5525170884,2.4724178105,-2.1533602293
H,0,4.0384913656,0.5233074247,2.4024788138
H,0,3.1532588356,-0.6705014774,1.4549682237
H,0,2.3361761969,0.2268594835,2.7506609317
N,0,0.3880880379,0.0730773907,-0.2550159791
O,0,0.4846511392,0.623010531,-1.2088380795
O,0,0.2145863121,-0.442721144,0.7094671887
F,0,2.0532083379,-2.5834674987,-2.6548032634
B,0,1.5610253326,-2.4204242908,-1.3754787311
F,0,0.1959900283,-2.0142984308,-1.4243862297
F,0,1.6852881721,-3.5672675835,-0.614976118
F,0,2.2448532861,-1.3402992757,-0.7266626054

Nitration of Toluene Including a Sulfuric Acid Molecule

The transition structures in this section were located in M06-2X/6-311G*/PCM calculations with δ=109.

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 3.45_370364*
m062x/6-311G*
E(RM062X) = -1176.50893228

Zero-point correction= 0.182468 (Hartree/Particle)
Thermal correction to Energy= 0.198253
Thermal correction to Enthalpy= 0.199197
Thermal correction to Gibbs Free Energy= 0.138569
Sum of electronic and ZPE= -1176.326464
Sum of electronic and thermal Energies= -1176.310679
Sum of electronic and thermal Enthalpies= -1176.309735
Sum of electronic and thermal Free Energies= -1176.370364

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	124.406	56.282	127.604

C,0,1.3698326556,0.0182068278,1.4911963992
C,0,2.5899498691,-1.3255273713,-0.6470028025
C,0,2.5940893992,0.4706352542,0.9465071895
C,0,0.7850171121,-1.1386896379,0.9525362602
C,0,3.2089348477,-0.2115676862,-0.1023284159
C,0,1.3770795171,-1.7899398491,-0.1128843569
C,0,0.7390432258,0.7231195096,2.6549407415
H,0,3.0407593302,-1.8429758482,-1.4853334544
H,0,3.0653574329,1.3518361486,1.3710279924
H,0,-0.1445732827,-1.5073785323,1.3724876921
H,0,4.1478659522,0.148454098,-0.5043464175
H,0,0.8992693438,-2.6610971288,-0.5449385977
N,0,0.7211368096,1.566735618,-0.3987408832
O,0,0.7166108908,0.906855788,-1.3075953998
O,0,0.5326120611,2.4831485281,0.2294796734
S,0,-2.4736213367,-0.2006640567,-0.2076509075
O,0,-1.6137190458,-1.004965783,-1.2627611712
O,0,-2.6152763146,-1.2079812018,1.0015424144
O,0,-3.7639241745,0.1036251227,-0.7479302073
O,0,-1.5879778941,0.8219883888,0.2705558856
H,0,-3.3619253283,-1.823071045,0.9167004716
H,0,-2.1352756725,-1.5760798946,-1.8497466355
H,0,0.9970519161,0.2022755461,3.5811898657
H,0,1.0977454939,1.749088853,2.7505217536
H,0,-0.348702808,0.7294223517,2.5667709102

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 3.42_370300*
m062x/6-311G*
E(RM062X) = -1176.50889413

Zero-point correction= 0.182381 (Hartree/Particle)
Thermal correction to Energy= 0.198114
Thermal correction to Enthalpy= 0.199058
Thermal correction to Gibbs Free Energy= 0.138594
Sum of electronic and ZPE= -1176.326513
Sum of electronic and thermal Energies= -1176.310780
Sum of electronic and thermal Enthalpies= -1176.309836
Sum of electronic and thermal Free Energies= -1176.370300

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.318 56.277 127.257

C,0,1.2896093973,-0.0464573232,1.45272334
C,0,2.6550744219,-1.3535333857,-0.625937531
C,0,2.499232734,0.4696367623,0.9287105508
C,0,0.786408799,-1.2356836003,0.9118388947
C,0,3.1923251081,-0.1989456589,-0.0817417674
C,0,1.4483104282,-1.8679490353,-0.1267989498
C,0,0.6069055638,0.6403404102,2.5973056112
H,0,3.1628907709,-1.8620530078,-1.4364668036
H,0,2.9076929475,1.3826906203,1.3516899088
H,0,-0.1348646109,-1.6511579069,1.3043400249
H,0,4.1246637266,0.2063122471,-0.4550082315
H,0,1.0313890275,-2.769715771,-0.5598021815
N,0,0.7331289131,1.47343085,-0.5546129554
O,0,0.6922168606,0.7363151395,-1.40072942
O,0,0.5760197374,2.4443930554,-0.0046960422
S,0,-2.5146102658,-0.1972536271,-0.027546193
O,0,-1.7738866623,-1.1599251811,-1.0394291764
O,0,-2.5734654388,-1.0379761449,1.3098029412
O,0,-3.8403722439,0.0830171506,-0.4894992455
O,0,-1.5650632966,0.8439824497,0.2392611957
H,0,-3.3429942107,-1.6269909727,1.3724551751
H,0,-2.3599207049,-1.7843090339,-1.4971480685
H,0,1.1304754874,0.40677344,3.5284774831
H,0,0.6310003855,1.7276022352,2.4871356241
H,0,-0.429244875,0.3183642884,2.6921748161

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 3.41_370239*
m062x/6-311G*
E(RM062X) = -1176.50813056

Zero-point correction= 0.182483 (Hartree/Particle)
Thermal correction to Energy= 0.198280
Thermal correction to Enthalpy= 0.199224
Thermal correction to Gibbs Free Energy= 0.137891
Sum of electronic and ZPE= -1176.325648
Sum of electronic and thermal Energies= -1176.309851

Sum of electronic and thermal Enthalpies= -1176.308907
Sum of electronic and thermal Free Energies= -1176.370239

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.422 56.198 129.085

C,0,1.3192603856,-0.0574419201,1.464644467
C,0,2.665139579,-1.3432928232,-0.6425476287
C,0,2.5160913703,0.4714784346,0.923054857
C,0,0.8191013379,-1.2488871114,0.9256319627
C,0,3.2023984729,-0.1898217369,-0.0986145123
C,0,1.4699306077,-1.8698081535,-0.126912706
C,0,0.647189778,0.6170336186,2.6221405683
H,0,3.1632125906,-1.8437464535,-1.4639492006
H,0,2.9258615469,1.3837004103,1.3463805772
H,0,-0.0856939709,-1.681977874,1.3384540709
H,0,4.1260767193,0.2248704597,-0.4826999663
H,0,1.0560534081,-2.7753207518,-0.5551313111
N,0,0.7784556459,1.4961839707,-0.5281052404
O,0,0.7100447106,0.7669805789,-1.3807276458
O,0,0.6330934374,2.4686636714,0.0243601844
S,0,-2.4126198876,-0.2152591959,0.1449491901
O,0,-1.8475892434,-1.0417161677,-1.0795586929
O,0,-2.6408870744,-1.0854888126,1.2616294104
O,0,-3.7822862796,0.3613850718,-0.38278063
O,0,-1.5376748886,0.9165451346,0.2455844139
H,0,-4.5407127391,-0.2251157614,-0.2295320171
H,0,-2.2165559644,-1.9364763584,-1.1621386398
H,0,1.181977764,0.3769430016,3.5452161407
H,0,0.6651695171,1.7050640689,2.5208113836
H,0,-0.3864828231,0.2896156993,2.7274249649

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 3.44_370143*
m062x/6-311G*
E(RM062X) = -1176.50824968

Zero-point correction= 0.182460 (Hartree/Particle)
Thermal correction to Energy= 0.198238
Thermal correction to Enthalpy= 0.199182
Thermal correction to Gibbs Free Energy= 0.138107
Sum of electronic and ZPE= -1176.325789
Sum of electronic and thermal Energies= -1176.310012
Sum of electronic and thermal Enthalpies= -1176.309067
Sum of electronic and thermal Free Energies= -1176.370143

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.396 56.166 128.544

C,0,1.3772607127,0.0120189635,1.5014506462
C,0,2.5807194907,-1.340933762,-0.6419454989
C,0,2.5600179472,0.5003584927,0.8986639033
C,0,0.8268428595,-1.1860931251,1.0180598905
C,0,3.1690577184,-0.187264205,-0.1512847688
C,0,1.4087854916,-1.841583617,-0.0499525105
C,0,0.7587134538,0.7222472444,2.6679510624
H,0,3.0235529982,-1.8640071945,-1.4809596429
H,0,3.0070587524,1.4128854535,1.281033254
H,0,-0.0664511689,-1.5859199104,1.4867762148
H,0,4.077588265,0.1999454197,-0.5955925424
H,0,0.9589062347,-2.7482927333,-0.4368036722
N,0,0.6320262879,1.487948704,-0.4076070606
O,0,0.6085050705,0.8007559305,-1.2967766779
O,0,0.4345264432,2.4217196343,0.1932109351
S,0,-2.4386267361,-0.449940583,0.0520734533
O,0,-1.7555697949,-1.0919547737,-1.2217763486
O,0,-2.6772330264,-1.4590667182,1.0419713208
O,0,-3.8080510151,0.111798337,-0.4922057014
O,0,-1.64107296,0.7079999921,0.3376562814
H,0,-4.5362867182,-0.5295685407,-0.4601985373
H,0,-2.0587895924,-1.9917470298,-1.4259070134
H,0,1.0605134407,0.2291791595,3.5961748331
H,0,1.0873236107,1.7605823447,2.7305800184
H,0,-0.3307677655,0.6929085168,2.6131811616

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 3.46_370093*
m062x/6-311G*
E(RM062X) = -1176.50757660

Zero-point correction= 0.182598 (Hartree/Particle)
Thermal correction to Energy= 0.198434
Thermal correction to Enthalpy= 0.199379
Thermal correction to Gibbs Free Energy= 0.137484
Sum of electronic and ZPE= -1176.324979
Sum of electronic and thermal Energies= -1176.309142
Sum of electronic and thermal Enthalpies= -1176.308198
Sum of electronic and thermal Free Energies= -1176.370093

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.520 56.117 130.268

C,0,1.3848620334,0.0290383966,1.5069950078
C,0,2.5867102601,-1.3253173034,-0.6351977056
C,0,2.6188747783,0.4609716968,0.9704829222
C,0,0.7837427465,-1.1178298372,0.962173494
C,0,3.2240994008,-0.2265681915,-0.0810832119
C,0,1.3656815084,-1.7739399677,-0.1055320323
C,0,0.7533351081,0.7422114696,2.6654340651

H,0,3.0312379998,-1.8456719895,-1.4750707434
H,0,3.105087154,1.3311453047,1.4004590576
H,0,-0.1487209234,-1.4762935517,1.3857014382
H,0,4.1709409849,0.11811688,-0.4780310821
H,0,0.87608982,-2.6369851287,-0.5405432009
N,0,0.7646321665,1.6035632932,-0.3757379748
O,0,0.7797579269,0.9560178475,-1.2931681569
O,0,0.5655177477,2.506643153,0.2666164004
S,0,-2.3306739583,-0.2437026587,-0.3217590812
O,0,-1.7845358479,-1.1048442768,-1.3301453991
O,0,-2.7641249993,-1.0915664957,0.9392309991
O,0,-3.6780388901,0.4041512115,-0.8223708262
O,0,-1.567567074,0.8453653336,0.2190395463
H,0,-3.1334527834,-1.9631635245,0.7224083616
H,0,-4.1858688527,-0.1565359382,-1.4309680176
H,0,0.9346150909,0.1796474853,3.5852836517
H,0,1.1718980744,1.7398650899,2.8040936088
H,0,-0.3278114714,0.820673702,2.533065879

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 3.43_369922*
m062x/6-311G*
E(RM062X) = -1176.50753881

Zero-point correction= 0.182345 (Hartree/Particle)
Thermal correction to Energy= 0.198187
Thermal correction to Enthalpy= 0.199131
Thermal correction to Gibbs Free Energy= 0.137617
Sum of electronic and ZPE= -1176.325193
Sum of electronic and thermal Energies= -1176.309352
Sum of electronic and thermal Enthalpies= -1176.308408
Sum of electronic and thermal Free Energies= -1176.369922

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.364 56.256 129.468

C,0,1.2356313461,-2.0638017922,1.0980799472
C,0,3.28809509,-0.8672120359,-0.3361021218
C,0,1.4209414079,-0.6963756079,1.1910857181
C,0,2.0906581285,-2.847513665,0.3064154189
C,0,2.4366496239,-0.0643935603,0.4604456658
C,0,3.1324573218,-2.2532553507,-0.3860338494
H,0,0.4262129361,-2.5355760427,1.6425301782
H,0,4.0939216986,-0.3925389455,-0.8878343759
H,0,0.7788552522,-0.100995869,1.8302420737
H,0,1.9341221421,-3.9175099001,0.2431636589
C,0,2.6612747547,1.4135432414,0.5684120398
H,0,3.8030696639,-2.8496606407,-0.9920507362
N,0,1.3674431689,-0.283383964,-1.8523078481
O,0,0.7192059899,-1.1962028107,-1.7527515249

O,0,1.7627546045,0.6692987718,-2.3073577681
S,0,-1.4387591055,0.9826602834,0.1832064153
O,0,-1.8812427779,-0.3223801846,0.5789578596
O,0,-0.9502828136,1.7933386948,1.450922699
O,0,-2.6504183125,1.8303333467,-0.3644387819
O,0,-0.3875159307,1.1592020706,-0.7767175808
H,0,-3.5019860867,1.6121687968,0.0486700994
H,0,-1.4708944577,1.6278268674,2.2538183258
H,0,3.4335710916,1.6107289721,1.3173436136
H,0,3.0175585126,1.8379129998,-0.3730433382
H,0,1.7513867512,1.9312283244,0.871590212

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 3.46_369483*
m062x/6-311G*
E(RM062X) = -1176.50823352

Zero-point correction= 0.182931 (Hartree/Particle)
Thermal correction to Energy= 0.198567
Thermal correction to Enthalpy= 0.199511
Thermal correction to Gibbs Free Energy= 0.138751
Sum of electronic and ZPE= -1176.325303
Sum of electronic and thermal Energies= -1176.309666
Sum of electronic and thermal Enthalpies= -1176.308722
Sum of electronic and thermal Free Energies= -1176.369483

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.603 56.035 127.881

C,0,-0.2180113637,-0.1126305268,0.1802629739
C,0,0.3424060906,0.3065852992,2.8883152504
C,0,1.1164260489,-0.0452716501,0.6383155167
C,0,-1.2637689474,0.0857346119,1.1068190417
C,0,1.3911183545,0.1622877867,1.981841526
C,0,-0.9860071472,0.2816401352,2.4467414479
C,0,-0.523012904,-0.2797282672,-1.2776102735
H,0,0.5559327187,0.4479907321,3.9412499018
H,0,1.9259258497,-0.1668930112,-0.0739010462
H,0,-2.2902194855,0.0719895234,0.7565812467
H,0,2.4170451447,0.1949099367,2.3272358604
H,0,-1.7960646639,0.4140849958,3.1542404267
N,0,-0.0508388814,-2.4795270392,0.8678731912
O,0,0.0939673567,-2.4907770615,1.9830529681
O,0,-0.1789248807,-2.9045203753,-0.1693899789
S,0,-3.3627752532,-2.4236822665,2.3141267481
O,0,-2.4169375421,-2.612282905,3.5682324851
O,0,-4.0247686248,-1.1535562514,2.3886856836
O,0,-4.414012081,-3.5911866857,2.450365735
O,0,-2.5415107099,-2.7810905869,1.1930591711
H,0,-5.190925217,-3.3591328703,2.9846338586

H,0,-2.7657760184,-2.2331677475,4.3914090888
H,0,-0.6658188957,0.704403524,-1.7326805234
H,0,0.2927110129,-0.7725277751,-1.8079532678
H,0,-1.4446129607,-0.8448025253,-1.430524032

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 3.46_369466*
m062x/6-311G*
E(RM062X) = -1176.50823358

Zero-point correction= 0.182934 (Hartree/Particle)
Thermal correction to Energy= 0.198569
Thermal correction to Enthalpy= 0.199513
Thermal correction to Gibbs Free Energy= 0.138768
Sum of electronic and ZPE= -1176.325300
Sum of electronic and thermal Energies= -1176.309665
Sum of electronic and thermal Enthalpies= -1176.308721
Sum of electronic and thermal Free Energies= -1176.369466

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.604 56.034 127.849

C,0,1.1223484806,-1.4486463115,1.1981616853
C,0,3.3522312733,-1.0312245389,-0.4300078128
C,0,1.6854665978,-0.1883762866,1.1235312701
C,0,1.6664662364,-2.502005332,0.4534159251
C,0,2.793472644,0.0522640414,0.2833623755
C,0,2.7908594794,-2.2965513705,-0.3439892793
H,0,0.2597581439,-1.6200186513,1.8313047162
H,0,4.2227688108,-0.8594496239,-1.0545007027
H,0,1.2733930678,0.6307732153,1.7028799772
H,0,1.2148361598,-3.485694278,0.5048555919
C,0,3.4274977546,1.4096648036,0.2406655957
H,0,3.2150460949,-3.1179067984,-0.9081951792
N,0,1.2861131834,0.2102248444,-1.6674738973
O,0,0.678113685,-0.7354951924,-1.693394278
O,0,1.6380124012,1.2306737396,-1.9957905964
S,0,-1.587938157,0.8027673121,0.4426646838
O,0,-1.8850446015,-0.6147955595,-0.1938826122
O,0,-1.4003494101,0.6723935427,1.8585899124
O,0,-2.8928848116,1.6360961444,0.1436636017
O,0,-0.5752077512,1.3665879583,-0.403201941
H,0,-3.5782235284,1.5500657725,0.8261545267
H,0,-2.4164259186,-1.2012505984,0.3689124387
H,0,2.6813353016,2.2018387017,0.3286367614
H,0,4.1145477064,1.5150093666,1.0849764295
H,0,4.0036611574,1.5587610989,-0.6732961922

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 3.41_369431*
m062x/6-311G*

E(RM062X) = -1176.50796125

Zero-point correction= 0.182600 (Hartree/Particle)
Thermal correction to Energy= 0.198286
Thermal correction to Enthalpy= 0.199230
Thermal correction to Gibbs Free Energy= 0.138530
Sum of electronic and ZPE= -1176.325362
Sum of electronic and thermal Energies= -1176.309676
Sum of electronic and thermal Enthalpies= -1176.308731
Sum of electronic and thermal Free Energies= -1176.369431

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.426 56.076 127.753

C,0,1.6935849268,-0.0488377843,1.3751181221
C,0,2.3071921671,-1.3308718179,-1.0494263994
C,0,3.0325735634,-0.3260155166,1.0077240719
C,0,0.6723333934,-0.4283545046,0.4960903578
C,0,3.3325300127,-0.9922094361,-0.1823472755
C,0,0.9770263366,-1.0447141656,-0.7063265994
C,0,1.3887835579,0.5887865398,2.6981685075
H,0,2.5270620281,-1.8199232042,-1.9906857426
H,0,3.8330557271,-0.0551175613,1.6900546743
H,0,-0.3589216442,-0.2249526291,0.7605862834
H,0,4.3629481289,-1.2129973849,-0.4318441065
H,0,0.1790369257,-1.3144784519,-1.388109288
N,0,2.6299180279,1.9145798219,-0.03810725
O,0,2.2972111521,1.6371619076,-1.073687291
O,0,3.0180334575,2.5652739116,0.7963834255
S,0,-0.9785961719,2.8782676368,1.0805579929
O,0,-1.7571749663,1.7309211821,1.4311784093
O,0,-0.89843469,3.7446742479,2.3987109964
O,0,-1.7620540179,3.8008368484,0.0674283074
O,0,0.3313182402,2.7453395257,0.5071568683
H,0,-2.7087394423,3.8836992547,0.2679892228
H,0,-0.3063524559,4.5112020053,2.3274826336
H,0,1.8606438514,1.5721744021,2.7918164698
H,0,0.3150281117,0.708149629,2.8402293785
H,0,1.7803067802,-0.0251214561,3.512126231

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 2.46_368778*
m062x/6-311G*
E(RM062X) = -1176.50700707

Zero-point correction= 0.182525 (Hartree/Particle)
Thermal correction to Energy= 0.198277
Thermal correction to Enthalpy= 0.199221
Thermal correction to Gibbs Free Energy= 0.138229
Sum of electronic and ZPE= -1176.324482

Sum of electronic and thermal Energies= -1176.308730
Sum of electronic and thermal Enthalpies= -1176.307786
Sum of electronic and thermal Free Energies= -1176.368778

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.421 56.105 128.370

C,0,1.3946979783,-0.0557317179,1.4106703258
C,0,2.5965104742,-1.3471213873,-0.7668013543
C,0,2.7012776845,0.2622481542,1.0434316612
C,0,0.7174835086,-1.073308511,0.7045850326
C,0,3.2983369615,-0.360627795,-0.0446633928
C,0,1.3151493467,-1.7319461181,-0.3520101919
C,0,0.7040874993,0.6785930168,2.5193367303
H,0,3.0756464489,-1.8490913124,-1.5997397348
H,0,3.2475641528,1.0144773191,1.6019276877
H,0,-0.2917084246,-1.3369431089,1.0031503886
H,0,4.3042575434,-0.0887561973,-0.3445837785
H,0,0.7874051077,-2.5155296604,-0.8815680512
N,0,1.8749467474,0.6908139326,-1.9502585436
O,0,0.9915638252,1.0290934874,-1.3422776891
O,0,2.5873814247,0.6680569707,-2.8243024294
S,0,2.7605797852,3.5474474246,0.042068451
O,0,1.5746869327,3.2612473783,0.7894117996
O,0,3.930781786,3.5640422298,1.1046720636
O,0,2.7409294207,5.0240329851,-0.51329426
O,0,3.1385779666,2.7368793158,-1.0842639486
H,0,2.3892413696,5.6729105098,0.11798914
H,0,4.815303293,3.6462366356,0.7115308755
H,0,1.4169547004,1.216941569,3.1432532544
H,0,0.0127237386,1.4128390861,2.0962990254
H,0,0.1253637288,-0.0046472067,3.1429129384

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 2.46_368547*
m062x/6-311G*
E(RM062X) = -1176.50468519

Zero-point correction= 0.181786 (Hartree/Particle)
Thermal correction to Energy= 0.197922
Thermal correction to Enthalpy= 0.198867
Thermal correction to Gibbs Free Energy= 0.136138
Sum of electronic and ZPE= -1176.322899
Sum of electronic and thermal Energies= -1176.306763
Sum of electronic and thermal Enthalpies= -1176.305819
Sum of electronic and thermal Free Energies= -1176.368547

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.198 56.454 132.023

C,0,1.2677255647,-0.2738113823,1.1842970915
C,0,3.3604761659,-1.1187237732,-0.4852835656
C,0,2.4883613582,0.433587296,1.1438574021
C,0,1.117005835,-1.4337782834,0.4174886517
C,0,3.5283672382,-0.0015637461,0.3237503146
C,0,2.1397461266,-1.8300640224,-0.4200544269
H,0,0.4717936477,0.048598038,1.846312348
C,0,4.4389908761,-1.588171053,-1.4157146455
H,0,2.6190970015,1.3113739766,1.767095726
H,0,0.1954082149,-1.9998656946,0.4680226282
H,0,4.4617046005,0.54891241,0.3022518279
H,0,2.0156950593,-2.7096314183,-1.0433804186
N,0,0.9721990184,1.4067789076,-0.5897857242
O,0,1.2662112358,0.8318816188,-1.5125912917
O,0,0.5323986874,2.2765095201,-0.0168767976
S,0,-2.3363193718,-0.187245601,0.1195295487
O,0,-3.1224700733,-1.2060879069,-0.7948549798
O,0,-1.9855159743,-0.8142940557,1.3620710599
O,0,-3.3764328134,0.9731326461,0.3758106407
O,0,-1.3382781929,0.3848391195,-0.7348653401
H,0,-3.9922167858,0.7945459141,1.1050597592
H,0,-3.6628099414,-1.8419513464,-0.2989843191
H,0,4.704205127,-2.6254043464,-1.1984645768
H,0,4.0895756932,-1.554575751,-2.4505349132
H,0,5.3352407023,-0.975150066,-1.3330769994

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 3.45_368434*
m062x/6-311G*
E(RM062X) = -1176.50729410

Zero-point correction= 0.182563 (Hartree/Particle)
Thermal correction to Energy= 0.198250
Thermal correction to Enthalpy= 0.199194
Thermal correction to Gibbs Free Energy= 0.138860
Sum of electronic and ZPE= -1176.324731
Sum of electronic and thermal Energies= -1176.309044
Sum of electronic and thermal Enthalpies= -1176.308100
Sum of electronic and thermal Free Energies= -1176.368434

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.404 56.087 126.985

C,0,1.3100653065,-0.0525074452,1.4020342769
C,0,2.750095371,-1.2779419147,-0.6710712871
C,0,2.5649921709,0.4509845922,0.9856086631
C,0,0.8106838299,-1.2042044967,0.7724871446
C,0,3.2892139805,-0.1750267281,-0.0283800861
C,0,1.5096854864,-1.7953101939,-0.2628001386

C,0,0.565635967,0.584895985,2.536424248
H,0,3.2867425216,-1.7495844079,-1.4853465359
H,0,2.9735896278,1.3242889725,1.4846598671
H,0,-0.1291553263,-1.6282787846,1.1095092169
H,0,4.2508217575,0.2218291509,-0.3294233621
H,0,1.101241392,-2.6665396163,-0.7613046679
N,0,0.8228566282,1.5748990957,-0.4767126438
O,0,0.9268161118,0.9635723329,-1.4140399804
O,0,0.5442398906,2.4578814559,0.1666575797
S,0,-2.467121347,-0.3016936189,0.0147883296
O,0,-2.0677696494,-1.503190713,-0.9323465655
O,0,-2.6289233234,-0.8767920607,1.3104927842
O,0,-3.9097884639,0.1075937761,-0.4722429497
O,0,-1.5620863099,0.7983580926,-0.2069334373
H,0,-3.9155642702,0.7284046269,-1.2190875323
H,0,-1.7419664325,-1.2361028878,-1.8073600897
H,0,0.8600079755,0.1098692429,3.4766020966
H,0,0.7987612757,1.6472455136,2.6283190562
H,0,-0.5122121704,0.4610820309,2.4231120137

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 2.45_368346*
m062x/6-311G*
E(RM062X) = -1176.50607699

Zero-point correction= 0.182224 (Hartree/Particle)
Thermal correction to Energy= 0.198085
Thermal correction to Enthalpy= 0.199029
Thermal correction to Gibbs Free Energy= 0.137731
Sum of electronic and ZPE= -1176.323853
Sum of electronic and thermal Energies= -1176.307992
Sum of electronic and thermal Enthalpies= -1176.307048
Sum of electronic and thermal Free Energies= -1176.368346

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.300 56.231 129.012

C,0,1.2951943995,-0.4934208794,1.3829299282
C,0,3.1982355277,-1.2049080253,-0.5411415225
C,0,2.6099500371,0.0061859866,1.4654221616
C,0,0.9585112498,-1.410473959,0.3765303891
C,0,3.5484368367,-0.3521059492,0.5093468865
C,0,1.8955192641,-1.7406820081,-0.5820501736
H,0,0.5633492242,-0.2226839373,2.1345611248
C,0,4.1788235132,-1.5400680491,-1.6249973408
H,0,2.8775470183,0.677800256,2.273178504
H,0,-0.0356893642,-1.8397851307,0.3445010875
H,0,4.5554579218,0.045490518,0.5644607902
H,0,1.6319179568,-2.4213739795,-1.3844616387
N,0,0.9888057256,1.4647454521,-0.0574557741

O,0,1.4882848939,1.1818888097,-1.0230037291
O,0,0.4007470691,2.1030531493,0.6634276309
S,0,-2.2983802868,0.0875322091,-0.3112001854
O,0,-2.4071564182,-1.4614062512,-0.6003856389
O,0,-1.8009167758,0.1441111727,1.1925477233
O,0,-3.5843261383,0.7041431221,-0.4297248773
O,0,-1.1630333909,0.5268684789,-1.0693149528
H,0,-2.5119310556,0.1239172018,1.8531946275
H,0,-3.2504928699,-1.8544101805,-0.3222362388
H,0,3.9678276614,-0.9383741554,-2.5141856442
H,0,5.2032440839,-1.3351756744,-1.3158345241
H,0,4.0985689166,-2.5884161774,-1.9162286134

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 2.44_368221*
m062x/6-311G*
E(RM062X) = -1176.50532400

Zero-point correction= 0.182100 (Hartree/Particle)
Thermal correction to Energy= 0.198138
Thermal correction to Enthalpy= 0.199083
Thermal correction to Gibbs Free Energy= 0.137103
Sum of electronic and ZPE= -1176.323224
Sum of electronic and thermal Energies= -1176.307186
Sum of electronic and thermal Enthalpies= -1176.306241
Sum of electronic and thermal Free Energies= -1176.368221

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.334 56.382 130.447

C,0,1.2042125192,-0.1373309213,1.4380541965
C,0,2.7287361883,-1.0708580895,-0.7161641512
C,0,2.4202322414,0.4722254201,1.1258366128
C,0,0.7891810188,-1.2589440339,0.6901726644
C,0,3.1744399643,0.0263039244,0.0492876823
C,0,1.5524052058,-1.7426040163,-0.3536017168
C,0,0.3355392341,0.3944457811,2.538067218
H,0,3.3353887364,-1.4371144579,-1.5363768167
H,0,2.7704354133,1.3059993972,1.7231395369
H,0,-0.14610799,-1.7448121896,0.9468186123
H,0,4.1070835091,0.5182036409,-0.2050004504
H,0,1.2290966048,-2.6097319546,-0.9162493125
N,0,1.593874083,0.7054541483,-1.9449699837
O,0,0.6607965344,0.8875092435,-1.3441673016
O,0,2.2947685133,0.7931075924,-2.8247902306
S,0,2.8695312951,3.6943825003,-0.0377849025
O,0,1.7513820532,3.6801233498,1.0812707905
O,0,4.0696991897,3.2889757421,0.6183467704
O,0,3.0487633572,5.2241942852,-0.3779655467
O,0,2.3771971457,3.0068427027,-1.2049979325

H,0,2.4129314165,5.5620379462,-1.0294884127
H,0,0.8437700641,3.7439112097,0.7423338876
H,0,-0.5215210551,0.9226790057,2.1095955364
H,0,-0.0582282917,-0.4158976999,3.1538932737
H,0,0.8792520491,1.0924794735,3.1736119761

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 3.42_368199*
m062x/6-311G*
E(RM062X) = -1176.50519050

Zero-point correction= 0.182050 (Hartree/Particle)
Thermal correction to Energy= 0.198019
Thermal correction to Enthalpy= 0.198963
Thermal correction to Gibbs Free Energy= 0.136991
Sum of electronic and ZPE= -1176.323141
Sum of electronic and thermal Energies= -1176.307172
Sum of electronic and thermal Enthalpies= -1176.306228
Sum of electronic and thermal Free Energies= -1176.368199

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.259 56.397 130.430

C,0,1.1922289591,-0.6843599428,1.4325987854
C,0,3.2683159534,-1.215575417,-0.373339391
C,0,2.1282355489,0.3036827796,1.1181572445
C,0,1.2647407505,-1.9140191107,0.8025061283
C,0,3.1936467409,0.0491930522,0.2247052759
C,0,2.3060141876,-2.1749843787,-0.1036672
H,0,0.401122122,-0.468774656,2.1397801341
H,0,4.0750544431,-1.4328258682,-1.0643051275
H,0,2.0617369677,1.276648808,1.5955903046
H,0,0.5225380192,-2.6765968944,1.0067336745
C,0,4.2409875695,1.0969708745,-0.0172981801
H,0,2.3585684744,-3.140612582,-0.5924572876
N,0,1.1582276499,0.9092461963,-1.1253243353
O,0,0.751211123,-0.0665269275,-1.5019250919
O,0,1.339245627,2.0200285593,-1.0758366194
S,0,-2.0448105084,0.1474984983,0.1858626066
O,0,-1.9792681624,-0.9616770381,-0.7218497451
O,0,-2.1273652885,-0.3803154106,1.6733427557
O,0,-3.3978062496,0.9350589946,-0.0086351873
O,0,-1.0209514659,1.1527428217,0.2035444459
H,0,-4.1435285451,0.3754802117,-0.2796086387
H,0,-2.6339664001,-1.2034289961,1.7716118579
H,0,5.0199448872,1.0150896562,0.7458144794
H,0,4.7117652646,0.9769012527,-0.9927123072
H,0,3.8277363322,2.1050575171,0.0576774181

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 2.43_368154*

m062x/6-311G*
E(RM062X) = -1176.50633068

Zero-point correction= 0.182762 (Hartree/Particle)
Thermal correction to Energy= 0.198529
Thermal correction to Enthalpy= 0.199473
Thermal correction to Gibbs Free Energy= 0.138177
Sum of electronic and ZPE= -1176.323569
Sum of electronic and thermal Energies= -1176.307802
Sum of electronic and thermal Enthalpies= -1176.306858
Sum of electronic and thermal Free Energies= -1176.368154

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.579 55.947 129.009

C,0,1.3246840153,-0.1352029004,1.4953650177
C,0,2.7387165081,-1.0877992152,-0.7213613676
C,0,2.5749911437,0.4040532847,1.1742321529
C,0,0.8246241528,-1.2073294265,0.7306843306
C,0,3.2784047467,-0.0565658818,0.0736997951
C,0,1.5303607644,-1.6987837113,-0.3494601539
C,0,0.5142014072,0.4348373339,2.6193409495
H,0,3.3002178138,-1.4644494736,-1.5684310657
H,0,2.9893381254,1.197662279,1.7857120253
H,0,-0.1309079015,-1.6454159618,0.9978578913
H,0,4.2375842458,0.3770324031,-0.186302691
H,0,1.1423531694,-2.5256480754,-0.9318095255
N,0,1.6109814073,0.7242692583,-1.8835224669
O,0,0.7820540325,1.0274151658,-1.1863087195
O,0,2.2144220707,0.720685632,-2.8370980506
S,0,2.8798789688,3.6392533307,-0.0613472209
O,0,1.465497718,3.4261103154,0.6170718576
O,0,3.9205152914,3.4293813308,0.9028126657
O,0,2.8610203596,5.1498406006,-0.5160395003
O,0,2.8120768667,2.8768114962,-1.2735618684
H,0,3.1598447812,5.7698803074,0.1691935635
H,0,1.4128337856,3.7343396761,1.5361553777
H,0,1.1422638731,0.9665545483,3.3340602336
H,0,-0.2136279072,1.1476622161,2.2184250196
H,0,-0.0436724388,-0.3429225323,3.1419597503

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 2.50_368101*
m062x/6-311G*
E(RM062X) = -1176.50660328

Zero-point correction= 0.182466 (Hartree/Particle)
Thermal correction to Energy= 0.198227
Thermal correction to Enthalpy= 0.199172
Thermal correction to Gibbs Free Energy= 0.138502

Sum of electronic and ZPE= -1176.324137
Sum of electronic and thermal Energies= -1176.308376
Sum of electronic and thermal Enthalpies= -1176.307432
Sum of electronic and thermal Free Energies= -1176.368101

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.390 56.181 127.690

C,0,1.4209347188,0.027249842,1.2521282174
C,0,3.0262519673,-1.36915888,-0.5691194524
C,0,2.6038563894,0.6119188228,0.7794803448
C,0,1.0829131423,-1.2839034426,0.8603522568
C,0,3.3761007297,-0.0702123026,-0.1383551524
C,0,1.8927441855,-1.9750320821,-0.032393294
H,0,0.7989240191,0.5530904252,1.9675038121
C,0,3.8634756162,-2.0621224218,-1.6012695572
H,0,2.8853912069,1.6050399858,1.1068862189
H,0,0.1850583869,-1.7473977008,1.2533437037
H,0,4.2699108996,0.3931738169,-0.5426270469
H,0,1.6296267319,-2.9852808747,-0.3268759235
N,0,0.0901106523,0.4669185759,-0.7539128971
O,0,0.8450712369,0.3953138682,-1.585149786
O,0,-0.9054714714,0.7097092376,-0.2794289196
S,0,-0.4892130776,-2.7512885288,-2.4542642478
O,0,0.7972221178,-2.1500227322,-3.1541983162
O,0,-0.2113353839,-4.0710991247,-1.9679701109
O,0,-1.5553383865,-2.8149490439,-3.6158626925
O,0,-0.9374959126,-1.7067351569,-1.5804414722
H,0,-1.5518338991,-3.6512432253,-4.1091053942
H,0,1.2976807333,-2.7869651871,-3.6898807178
H,0,3.6021907941,-3.1164867523,-1.6874335088
H,0,3.7136105982,-1.5907655766,-2.5769216432
H,0,4.9252420049,-1.9793425419,-1.3622174206

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 2.45_367948*
m062x/6-311G*
E(RM062X) = -1176.50450469

Zero-point correction= 0.181829 (Hartree/Particle)
Thermal correction to Energy= 0.197883
Thermal correction to Enthalpy= 0.198827
Thermal correction to Gibbs Free Energy= 0.136557
Sum of electronic and ZPE= -1176.322676
Sum of electronic and thermal Energies= -1176.306622
Sum of electronic and thermal Enthalpies= -1176.305677
Sum of electronic and thermal Free Energies= -1176.367948

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K

Total 124.174 56.404 131.059

C,0,1.3059363286,-0.1845987137,1.2828123849
C,0,3.2403817907,-1.1472512183,-0.5051910293
C,0,2.5830201518,0.4123182838,1.2161040466
C,0,1.0276354223,-1.3108393375,0.4982773232
C,0,3.5420096615,-0.0804244969,0.3365534623
C,0,1.9721283953,-1.7623325136,-0.4000588001
H,0,0.5663730354,0.1856507649,1.9843286106
C,0,4.2268661504,-1.6439763368,-1.5189879854
H,0,2.8138385954,1.2547861082,1.8586412284
H,0,0.0710170548,-1.8115147797,0.5875058612
H,0,4.5187713069,0.3866420195,0.2884584116
H,0,1.746508587,-2.6099756172,-1.0386802733
N,0,1.0441910742,1.5360102161,-0.4363517726
O,0,1.3451001538,1.009261321,-1.3855528605
O,0,0.6161424385,2.3839001207,0.1774183934
S,0,-2.2277599982,-0.1199904913,0.0266513479
O,0,-2.3729455343,-1.5781025794,-0.5661562289
O,0,-2.0098306692,-0.296494823,1.4263063841
O,0,-3.669956717,0.497998984,-0.1203601364
O,0,-1.3025234289,0.625676073,-0.7892432105
H,0,-3.8461096418,0.8897702495,-0.9910061353
H,0,-2.290924138,-1.6240978982,-1.532433674
H,0,4.2864787025,-2.7336684765,-1.5033891241
H,0,3.9076552916,-1.3513951521,-2.5234578006
H,0,5.2207559867,-1.2336097063,-1.3452494228

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 3.47_367776*
m062x/6-311G*
E(RM062X) = -1176.50698426

Zero-point correction= 0.182836 (Hartree/Particle)
Thermal correction to Energy= 0.198424
Thermal correction to Enthalpy= 0.199368
Thermal correction to Gibbs Free Energy= 0.139208
Sum of electronic and ZPE= -1176.324148
Sum of electronic and thermal Energies= -1176.308560
Sum of electronic and thermal Enthalpies= -1176.307616
Sum of electronic and thermal Free Energies= -1176.367776

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.513 56.060 126.617

C,0,-0.182898926,-0.093589264,0.1478782505
C,0,0.3931473862,0.2838510685,2.8589777528
C,0,1.1478579764,0.0823607856,0.5803498537
C,0,-1.2206688668,-0.0319894324,1.1034318987
C,0,1.4311847568,0.2623727671,1.9233062794

C,0,-0.9334493371,0.1517590681,2.4463386853
C,0,-0.503760729,-0.2381763031,-1.3093700668
H,0,0.6209526686,0.4102731504,3.9108282444
H,0,1.9489981806,0.0598309068,-0.1505886161
H,0,-2.2495395575,-0.1348760167,0.7757316867
H,0,2.4574912449,0.3745899585,2.2506634849
H,0,-1.7383809235,0.1824714693,3.1713306469
N,0,0.0222179876,-2.4833145884,0.7946158865
O,0,0.3511905142,-2.4997587352,1.8688177482
O,0,-0.2504508322,-2.8879587663,-0.221365092
S,0,-3.3678951491,-2.5495558824,2.4578000436
O,0,-2.7945882768,-2.7314956473,3.9192193287
O,0,-3.9283543994,-1.2380123837,2.4290685618
O,0,-4.5867089034,-3.5493208857,2.3958316638
O,0,-2.3714612,-2.9656659796,1.5022934272
H,0,-4.3415388109,-4.458593101,2.1588037408
H,0,-2.2317110873,-3.5147562033,4.0307173711
H,0,-0.6830539458,0.7506004181,-1.7408684724
H,0,0.3195290266,-0.6941680564,-1.8610638565
H,0,-1.4094417968,-0.827594347,-1.4638824513

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 2.45_367760*
m062x/6-311G*
E(RM062X) = -1176.50395742

Zero-point correction= 0.182287 (Hartree/Particle)
Thermal correction to Energy= 0.198322
Thermal correction to Enthalpy= 0.199266
Thermal correction to Gibbs Free Energy= 0.136197
Sum of electronic and ZPE= -1176.321671
Sum of electronic and thermal Energies= -1176.305636
Sum of electronic and thermal Enthalpies= -1176.304692
Sum of electronic and thermal Free Energies= -1176.367760

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.449 56.110 132.739

C,0,1.3018632539,-0.1069590375,1.4253909544
C,0,2.6765326666,-1.2914041261,-0.7101003457
C,0,2.5402480382,0.4082640586,0.9802268409
C,0,0.7899306157,-1.2501139068,0.8170435544
C,0,3.2358003697,-0.1894686532,-0.0502400537
C,0,1.4595871348,-1.8369861869,-0.2516315288
C,0,0.5763580161,0.579145547,2.5439588056
H,0,3.2072569701,-1.7642101539,-1.5288746884
H,0,2.9484290807,1.2876651275,1.4678287269
H,0,-0.1489287218,-1.6695924739,1.1595830508
H,0,4.2004478892,0.1948891451,-0.3590435659
H,0,1.0510268059,-2.7168743658,-0.7361209348

N,0,1.0219510261,-0.0683699724,-2.0417445636
O,0,0.7165186825,0.7836261389,-1.3725861015
O,0,1.0637572662,-0.6655426202,-2.9994356031
S,0,4.148870552,1.99399554,-2.6466277464
O,0,3.9974626988,2.8449404637,-1.3223211578
O,0,5.3228216402,1.2061194323,-2.4576513956
O,0,4.5070294565,3.0636623857,-3.7494194082
O,0,2.8798147884,1.3900457453,-2.9670260484
H,0,3.735332728,3.4952550458,-4.1504675623
H,0,3.1484705242,3.3088035421,-1.2381528913
H,0,1.202554912,0.6115551911,3.4386927359
H,0,0.3494423934,1.6127664785,2.2717516878
H,0,-0.3555827874,0.072132655,2.7892442388

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 2.47_367357*
m062x/6-311G*
E(RM062X) = -1176.50600394

Zero-point correction= 0.182633 (Hartree/Particle)
Thermal correction to Energy= 0.198369
Thermal correction to Enthalpy= 0.199313
Thermal correction to Gibbs Free Energy= 0.138647
Sum of electronic and ZPE= -1176.323371
Sum of electronic and thermal Energies= -1176.307635
Sum of electronic and thermal Enthalpies= -1176.306691
Sum of electronic and thermal Free Energies= -1176.367357

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.478 56.086 127.682

C,0,1.3857235316,-0.0896439679,1.4121306041
C,0,2.5741746083,-1.3639937917,-0.7834142686
C,0,2.6947737114,0.2198175953,1.0482161038
C,0,0.697322221,-1.0892383588,0.690776014
C,0,3.2856174939,-0.3944347943,-0.0484970196
C,0,1.2879474076,-1.73930518,-0.3749502189
C,0,0.7037855868,0.6369897831,2.5314591943
H,0,3.0480409627,-1.8598240505,-1.6230042323
H,0,3.2514587279,0.9577706327,1.6151789187
H,0,-0.3146626896,-1.346351207,0.985513736
H,0,4.293798451,-0.1273198392,-0.3449347164
H,0,0.7516617918,-2.5093189952,-0.9156664195
N,0,1.8885641938,0.7058700238,-1.9354796496
O,0,1.0043081385,1.0426100657,-1.327812362
O,0,2.6065300236,0.6901853504,-2.805045064
S,0,2.7671774618,3.5359844499,0.0790515572
O,0,1.5320728637,3.2868712974,0.765419974
O,0,3.9689188911,3.5112216628,1.1060336917
O,0,2.789055606,5.0057215991,-0.4940969171

O,0,3.1937973088,2.7002816633,-1.0057572645
H,0,2.3055558986,5.6483112926,0.0499572861
H,0,3.7530915684,3.8836898151,1.9764431761
H,0,1.4245717382,1.1426673308,3.1737204569
H,0,0.0354421802,1.3982199465,2.1189898056
H,0,0.1025783227,-0.0445903241,3.1350656142

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 2.47_367350*
m062x/6-311G*
E(RM062X) = -1176.50600378

Zero-point correction= 0.182637 (Hartree/Particle)
Thermal correction to Energy= 0.198371
Thermal correction to Enthalpy= 0.199315
Thermal correction to Gibbs Free Energy= 0.138654
Sum of electronic and ZPE= -1176.323367
Sum of electronic and thermal Energies= -1176.307633
Sum of electronic and thermal Enthalpies= -1176.306689
Sum of electronic and thermal Free Energies= -1176.367350

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.480 56.083 127.673

C,0,1.4474524532,0.0526059121,1.2664205643
C,0,3.0173548927,-1.3601478601,-0.5765056695
C,0,2.6056289584,0.6425367878,0.7442307153
C,0,1.1156323839,-1.2700918483,0.9105323047
C,0,3.3602682041,-0.0481276944,-0.1835099147
C,0,1.9088146606,-1.9683702355,0.0091701533
H,0,0.8406309888,0.5852658632,1.9898489187
C,0,3.8226672434,-2.068266077,-1.6233964974
H,0,2.88343263,1.6459103686,1.0424988425
H,0,0.2370776088,-1.7385726389,1.339860437
H,0,4.2349821926,0.419699491,-0.6229465824
H,0,1.653263105,-2.989174062,-0.2526825842
N,0,0.0411237165,0.4322830824,-0.7235611342
O,0,0.7841485968,0.3634874091,-1.5648342864
O,0,-0.9453861341,0.6536879006,-0.2239258657
S,0,-0.3687972422,-2.6539249343,-2.4975862442
O,0,0.8953987513,-2.3430040381,-3.1007167549
O,0,-0.2938585462,-4.0630596153,-1.7848343151
O,0,-1.4725296385,-2.8493403921,-3.6078676522
O,0,-0.9604427631,-1.781463843,-1.5249590145
H,0,-1.1348253288,-3.2227904718,-4.4380389815
H,0,0.2525420091,-4.7148305226,-2.2534420646
H,0,3.640456824,-3.1426064321,-1.6050326355
H,0,3.5385905636,-1.7003483446,-2.6134574814
H,0,4.8898188706,-1.8836658045,-1.4913102575

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 3.27_367301*
m062x/6-311G*
E(RM062X) = -1176.50416316

Zero-point correction= 0.182152 (Hartree/Particle)
Thermal correction to Energy= 0.198172
Thermal correction to Enthalpy= 0.199116
Thermal correction to Gibbs Free Energy= 0.136862
Sum of electronic and ZPE= -1176.322011
Sum of electronic and thermal Energies= -1176.305991
Sum of electronic and thermal Enthalpies= -1176.305047
Sum of electronic and thermal Free Energies= -1176.367301

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.355 56.279 131.025

C,0,1.175857137,-0.2923308959,1.2760808552
C,0,3.256935894,-1.2148096919,-0.3444163068
C,0,2.3045277143,0.5106309128,1.0189643123
C,0,1.0744619331,-1.5395044254,0.6854132724
C,0,3.3877698757,0.0356144552,0.2466906507
C,0,2.110318251,-1.9859302586,-0.1392942137
H,0,0.3868651978,0.0818033234,1.9172898212
H,0,4.0529342979,-1.5970580393,-0.9734843541
H,0,2.3860650659,1.4798176433,1.5011293721
H,0,0.2014809117,-2.157980262,0.855528096
C,0,4.6318567427,0.861640535,0.0887708816
H,0,2.0294324334,-2.9531533282,-0.6218482658
N,0,1.1556746024,1.2823394581,-0.9579864112
O,0,1.0959763618,0.3884333165,-1.6381960628
O,0,1.0217712819,2.3620164829,-0.6573072695
S,0,-2.2009761508,-0.089096922,0.130139374
O,0,-2.2647895056,-1.2632359659,-0.9254370796
O,0,-2.0326673396,-0.7238814542,1.3965676924
O,0,-3.6610400283,0.5079189903,0.1287692369
O,0,-1.2841925675,0.9197806311,-0.3384009061
H,0,-3.8067828379,1.1895883052,-0.5467203775
H,0,-2.1810032413,-0.9727228606,-1.8478667464
H,0,5.2659721767,0.7464305379,0.9719282741
H,0,5.2064790332,0.5490838709,-0.7824426008
H,0,4.3991867606,1.9237026415,-0.0061642448

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 3.08_366987*
m062x/6-311G*
E(RM062X) = -1176.50525318

Zero-point correction= 0.182356 (Hartree/Particle)
Thermal correction to Energy= 0.198117
Thermal correction to Enthalpy= 0.199061

Thermal correction to Gibbs Free Energy= 0.138266
Sum of electronic and ZPE= -1176.322897
Sum of electronic and thermal Energies= -1176.307136
Sum of electronic and thermal Enthalpies= -1176.306192
Sum of electronic and thermal Free Energies= -1176.366987

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.320 56.249 127.954

C,0,1.0642829031,-0.1910019511,0.8572016353
C,0,3.312362018,-1.3397429729,-0.4452653805
C,0,2.3328540429,0.3597195632,0.9946346116
C,0,0.9003634367,-1.288223651,0.0220877017
C,0,3.4413590385,-0.2130372422,0.3564197321
C,0,2.0167178283,-1.8411163596,-0.6523836985
H,0,0.2151280707,0.2396509746,1.3718170285
C,0,4.5180385257,-1.9874264648,-1.0643686397
H,0,2.4753463119,1.2374855904,1.6140559918
H,0,-0.0784372606,-1.7322427133,-0.1209177675
H,0,4.4223640161,0.2269759647,0.501958599
H,0,1.8753577834,-2.710917876,-1.2863424187
N,0,1.2054572961,-0.209110597,-2.2169007761
O,0,1.7056266123,0.7569320164,-1.9226136285
O,0,0.5864126765,-0.8750830344,-2.8915720119
S,0,3.6253354799,-1.79851512,-4.414825598
O,0,3.0852359611,-1.5563792946,-5.8775366202
O,0,4.9767125332,-2.2706116045,-4.4592989501
O,0,2.6717417416,-2.9279296006,-3.8423650219
O,0,3.2546458484,-0.6295941973,-3.6716464133
H,0,2.905026295,-3.8304408853,-4.113720406
H,0,3.4796541128,-2.1409146914,-6.5453541589
H,0,4.2434113916,-2.85559267,-1.6628975712
H,0,5.0602228877,-1.2814407428,-1.6959818175
H,0,5.2032574492,-2.3219254406,-0.2827334214

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 3.32_366879*
m062x/6-311G*
E(RM062X) = -1176.50595018

Zero-point correction= 0.182866 (Hartree/Particle)
Thermal correction to Energy= 0.198662
Thermal correction to Enthalpy= 0.199606
Thermal correction to Gibbs Free Energy= 0.139072
Sum of electronic and ZPE= -1176.323084
Sum of electronic and thermal Energies= -1176.307288
Sum of electronic and thermal Enthalpies= -1176.306344
Sum of electronic and thermal Free Energies= -1176.366879

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.662 56.151 127.406

C,0,1.1085620742,-0.2488348089,1.4023740487
C,0,3.1518427109,-1.2621083817,-0.2211803818
C,0,2.2033713882,0.5522548538,1.035904418
C,0,1.0153069306,-1.5368531384,0.9118139198
C,0,3.2665485885,0.0412639094,0.2570190922
C,0,2.0344528622,-2.0332234456,0.0874544274
H,0,0.3330840962,0.1599431148,2.038057263
H,0,3.9363028428,-1.6759184144,-0.8448183478
H,0,2.2770467127,1.5621893031,1.4274695401
H,0,0.1594390989,-2.1548347827,1.1527430666
C,0,4.481179254,0.8812240417,-0.0142754834
H,0,1.9556904546,-3.038829345,-0.3095784124
N,0,1.1332783534,1.1215136362,-1.0731729833
O,0,0.8970020257,0.139817299,-1.5657765739
O,0,1.1683828642,2.2438212077,-0.9588502661
S,0,-2.2148626553,0.0774294377,-0.0469725995
O,0,-1.6230199757,-1.1007051158,-0.9204570525
O,0,-2.0728862925,-0.4571432735,1.43435924
O,0,-3.5960679673,0.2832914669,-0.362753197
O,0,-1.2440237344,1.1278694997,-0.1538942252
H,0,-2.8142818676,-1.011637322,1.7270369958
H,0,-2.2561011444,-1.8085786006,-1.1218277369
H,0,4.9811131079,0.5747973144,-0.9326455636
H,0,4.2292610817,1.9408705657,-0.0850058499
H,0,5.1925601907,0.7736009782,0.8092736615

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 3.34_366676*
m062x/6-311G*
E(RM062X) = -1176.50534938

Zero-point correction= 0.182861 (Hartree/Particle)
Thermal correction to Energy= 0.198602
Thermal correction to Enthalpy= 0.199546
Thermal correction to Gibbs Free Energy= 0.138674
Sum of electronic and ZPE= -1176.322488
Sum of electronic and thermal Energies= -1176.306747
Sum of electronic and thermal Enthalpies= -1176.305803
Sum of electronic and thermal Free Energies= -1176.366676

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.625 55.982 128.117

C,0,1.2020189926,-0.3673889648,1.4445043513
C,0,3.1585399948,-1.2360862468,-0.3601711874

C,0,2.26455754,0.4742110407,1.0731457544
C,0,1.0951041214,-1.6195117654,0.8717464693
C,0,3.2870068187,0.0328136834,0.2021402096
C,0,2.0703576489,-2.0428199142,-0.0434254925
H,0,0.4631383183,-0.016510661,2.1545421113
H,0,3.910654614,-1.5938269046,-1.0542468703
H,0,2.3511420177,1.454272931,1.5318961228
H,0,0.2676986108,-2.2701471364,1.1274396267
C,0,4.4773181402,0.9041556419,-0.0765072292
H,0,1.9797550588,-3.0201301588,-0.5033758659
N,0,1.1061104328,1.190204373,-0.9362821885
O,0,0.8314569505,0.2454508869,-1.4799422906
O,0,1.1565987743,2.30268679,-0.7519469964
S,0,-2.0732472153,-0.0054145773,0.2829611131
O,0,-1.7304138191,-0.9318312735,-0.9536344531
O,0,-2.0681113214,-0.7837351706,1.4874049614
O,0,-3.529525979,0.5153984,-0.0226902064
O,0,-1.2221185471,1.138059927,0.1195889867
H,0,-4.2330820096,-0.0832787572,0.2763865461
H,0,-2.0638120255,-1.8404782009,-0.8769143972
H,0,5.2432340778,0.729554188,0.6842819888
H,0,4.9140514588,0.6835663236,-1.0501125788
H,0,4.2191583465,1.9637235459,-0.0352834852

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 2.48_366653*
m062x/6-311G*
E(RM062X) = -1176.50596937

Zero-point correction= 0.182740 (Hartree/Particle)
Thermal correction to Energy= 0.198294
Thermal correction to Enthalpy= 0.199238
Thermal correction to Gibbs Free Energy= 0.139316
Sum of electronic and ZPE= -1176.323229
Sum of electronic and thermal Energies= -1176.307675
Sum of electronic and thermal Enthalpies= -1176.306731
Sum of electronic and thermal Free Energies= -1176.366653

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.431 56.006 126.117

C,0,1.3522633047,-0.0195415153,1.3283820503
C,0,2.4465352315,-1.3946200832,-0.8624728545
C,0,2.6886480109,0.1607868421,0.9927535471
C,0,0.5779885775,-0.9257374524,0.5677011814
C,0,3.2326213324,-0.4995628256,-0.1077459176
C,0,1.1184970249,-1.6270947558,-0.4925057853
C,0,0.7170283771,0.7207420242,2.4669605349
H,0,2.8874005657,-1.9293940893,-1.6958976955
H,0,3.3126272491,0.8287991863,1.5762639826

H,0,-0.4635497268,-1.072192888,0.8344470906
H,0,4.2704265838,-0.3390381104,-0.3784169579
H,0,0.5120370379,-2.3258858961,-1.0550534411
N,0,2.1282205238,0.8182392138,-1.9410543308
O,0,1.172726589,1.1578002875,-1.452108971
O,0,2.9568936909,0.8271231435,-2.7078839766
S,0,2.6765281212,3.5683213891,0.2757722734
O,0,1.3493821715,3.2781854802,0.7367785152
O,0,3.6990798786,3.4652551397,1.4774410502
O,0,2.7784027408,5.0759025011,-0.1790232758
O,0,3.2766438857,2.8091451153,-0.7830626331
H,0,2.2087833678,5.6777477228,0.3272618995
H,0,3.3415503177,3.7648404766,2.3288265743
H,0,0.2213406114,0.0248487074,3.1471720193
H,0,1.450913145,1.3000518674,3.0259121401
H,0,-0.0401606122,1.4105025191,2.0870439805

Toluene / NO2+ / H2SO4 TS M06-2X/6-311G/PCM 3.33_365619*
m062x/6-311G*
E(RM062X) = -1176.50419780

Zero-point correction= 0.182762 (Hartree/Particle)
Thermal correction to Energy= 0.198553
Thermal correction to Enthalpy= 0.199497
Thermal correction to Gibbs Free Energy= 0.138579
Sum of electronic and ZPE= -1176.321436
Sum of electronic and thermal Energies= -1176.305645
Sum of electronic and thermal Enthalpies= -1176.304701
Sum of electronic and thermal Free Energies= -1176.365619

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.594 56.096 128.212

C,0,1.207224956,-0.4414402954,1.4662233836
C,0,3.1390746344,-1.2098816994,-0.4068561848
C,0,2.2535196544,0.4273434969,1.1132931721
C,0,1.1008799143,-1.6684487104,0.8412656855
C,0,3.2630487115,0.0365642126,0.2048673644
C,0,2.0645751596,-2.0414336336,-0.1070874676
H,0,0.4816607619,-0.1284310852,2.2066565655
H,0,3.8828303524,-1.5295296314,-1.1280714383
H,0,2.3364385553,1.3890684717,1.6100946494
H,0,0.2788376174,-2.3344208354,1.0735586102
C,0,4.4358107554,0.935824575,-0.0595665661
H,0,1.9755206664,-2.9985959642,-0.607843994
N,0,1.033508995,1.2009461916,-0.8525691503
O,0,0.7716523901,0.2700879486,-1.4253578422
O,0,1.0630472585,2.3043282633,-0.6205457089
S,0,-2.0950696249,-0.1538776196,0.1582897852

O,0,-1.764951982,-1.2195628577,-0.7306416733
O,0,-2.1323776797,-0.805157671,1.598485605
O,0,-3.5998150515,0.2256134325,-0.1242503018
O,0,-1.3031846286,1.052108745,0.2017037211
H,0,-3.8500033037,1.1107615924,0.187772152
H,0,-2.2903920892,-0.1765345613,2.3218731849
H,0,5.217330656,0.7447626661,0.6810955425
H,0,4.8589540773,0.759655083,-1.0481053643
H,0,4.1622962435,1.9888918858,0.0264342703

Nitration of Benzene Including a Sulfuric Acid Molecule

An exploratory series of calculations was performed to evaluate the system. This system includes an explicit molecule of sulfuric acid, in addition to benzene and NO_2^+. Some studies used water as the implicit solvent, while others, as marked, used δ=109. These calculations used M06-2X/6-311++G**.

Optimized TS for the nitration of benzene / H2SO4 in water
scrf=(solvent=water)
m062x/6-311++G**
E(RM062X) = -1137.22862808

Zero-point correction= 0.153518 (Hartree/Particle)
Thermal correction to Energy= 0.167849
Thermal correction to Enthalpy= 0.168793
Thermal correction to Gibbs Free Energy= 0.109978
Sum of electronic and ZPE= -1137.075110
Sum of electronic and thermal Energies= -1137.060779
Sum of electronic and thermal Enthalpies= -1137.059835
Sum of electronic and thermal Free Energies= -1137.118650

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	105.327	50.407	123.788

C,0,1.2433883745,-0.2428223357,1.1741211346
C,0,3.2943184877,-1.1350187881,-0.49811605
C,0,2.4466176734,0.4942952656,1.0452095581
C,0,1.0755898379,-1.4243688504,0.4586013985
C,0,3.4906760392,0.0142088326,0.2390290224
C,0,2.0844538117,-1.8496470019,-0.392629401
H,0,0.4608506769,0.1151282607,1.8337410466
H,0,4.0711679665,-1.499049796,-1.1587907331
H,0,2.5853451564,1.3932714356,1.6345974174
H,0,0.1603458322,-1.9953723859,0.555020991
H,0,4.4197906862,0.5654986479,0.1748355994
H,0,1.9498081449,-2.7498970189,-0.9801122743
N,0,1.1228535636,1.4545719814,-0.6344400695
O,0,1.2655007808,0.8176657575,-1.559305763
O,0,0.75964207,2.3989157682,-0.116817001

S,0,-2.2531235255,-0.1416098159,0.1329334456
O,0,-2.5308283627,-1.5123349896,-0.6079892351
O,0,-1.9476169669,-0.4902553231,1.4849294104
O,0,-3.6671070702,0.5625482192,0.1677795461
O,0,-1.3451991631,0.6484907141,-0.6615341492
H,0,-3.8703163879,1.0342564115,-0.6573255767
H,0,-2.5559936257,-1.4161329885,-1.5745903172

Optimized TS for the nitration of benzene / H2SO4 with eps=109
Scrf=(solvent=generic=read)
eps=109
epsinf=2.016
rsolv=2.5
m062x/6-311++G**
E(RM062X) = -1137.22898495

Zero-point correction= 0.153524 (Hartree/Particle)
Thermal correction to Energy= 0.167855
Thermal correction to Enthalpy= 0.168799
Thermal correction to Gibbs Free Energy= 0.109969
Sum of electronic and ZPE= -1137.075461
Sum of electronic and thermal Energies= -1137.061130
Sum of electronic and thermal Enthalpies= -1137.060186
Sum of electronic and thermal Free Energies= -1137.119016

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 105.331 50.401 123.819

C,0,1.242229262,-0.2448802291,1.1737812552
C,0,3.2950184823,-1.1345787946,-0.4977707368
C,0,2.444681072,0.493686734,1.0452197534
C,0,1.0757760891,-1.4260757829,0.4576120736
C,0,3.4899217265,0.0145488139,0.2397514058
C,0,2.0855476353,-1.8500807307,-0.393303153
H,0,0.45915009,0.1123503552,1.8331059991
H,0,4.072528475,-1.4978054547,-1.1580908063
H,0,2.5822941935,1.3925330657,1.6350247473
H,0,0.1609428559,-1.9978938175,0.5530424584
H,0,4.4184997629,0.5668119345,0.1762523485
H,0,1.951860377,-2.7500742962,-0.9813959988
N,0,1.1248023446,1.4540022475,-0.6340665089
O,0,1.2656724531,0.8166855998,-1.5590530862
O,0,0.7623867002,2.3993057846,-0.1173646692
S,0,-2.2535307302,-0.1414817273,0.133387552
O,0,-2.5324499553,-1.5105811573,-0.6099975757
O,0,-1.9493717504,-0.4929767513,1.4850282739
O,0,-3.6667661412,0.5642251148,0.1687845505
O,0,-1.3442351656,0.6489954291,-0.6590153533
H,0,-3.8686273514,1.0383106443,-0.6553063893

H,0,-2.5561664256,-1.4126849816,-1.5764781407

TS for the nitration of benzene / H2SO4 in water
scrf=(solvent=water)
m062x/6-311++G**
E(RM062X) = -1137.22726102

Zero-point correction= 0.154049 (Hartree/Particle)
Thermal correction to Energy= 0.166019
Thermal correction to Enthalpy= 0.166963
Thermal correction to Gibbs Free Energy= 0.114796
Sum of electronic and zero-point Energies= -1137.073212
Sum of electronic and thermal Energies= -1137.061242
Sum of electronic and thermal Enthalpies= -1137.060298
Sum of electronic and thermal Free Energies= -1137.112465

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 104.179 44.476 109.795

C,0,1.3808052492,-0.1790984205,1.2150657253
C,0,3.2485195488,-1.1046086776,-0.5984768334
C,0,2.6600428452,0.4238640053,1.1419762024
C,0,1.0813986765,-1.3063225731,0.4319121017
C,0,3.5902400313,-0.0471016994,0.2309442152
C,0,2.0014636881,-1.7434294623,-0.4902389748
H,0,0.6649692357,0.1701832907,1.9463477573
H,0,3.9581589183,-1.4563187812,-1.3349639493
H,0,2.8919539507,1.2578040922,1.7907612374
H,0,0.124883694,-1.7976488336,0.5427540226
H,0,4.562211449,0.4173184686,0.1530787729
H,0,1.7737778722,-2.5807993605,-1.1342095695
N,0,0.921870416,1.4081211505,-0.3438201047
O,0,1.2999043668,1.0488741651,-1.349674275
O,0,0.3454188767,2.1660555624,0.2810778143
S,0,-2.245054708,-0.0880996204,-0.0392357781
O,0,-2.5956427662,-1.5966039417,-0.2591598342
O,0,-1.7988912621,0.0159803287,1.3056628391
O,0,-3.6278408463,0.6344200468,-0.1015994545
O,0,-1.4174556668,0.364476163,-1.1158316087
H,0,-3.8800348189,0.8515530891,-1.0127155056
H,0,-2.6805347504,-1.8162769919,-1.2005068005

TS for the nitration of benzene / H2SO4 with eps=109
Scrf=(solvent=generic=read)
eps=109
epsinf=2.016
rsolv=2.5
m062x/6-311++G**
E(RM062X) = -1137.22760470

Zero-point correction= 0.154042 (Hartree/Particle)
Thermal correction to Energy= 0.166015
Thermal correction to Enthalpy= 0.166960
Thermal correction to Gibbs Free Energy= 0.114783
Sum of electronic and zero-point Energies= -1137.073563
Sum of electronic and thermal Energies= -1137.061589
Sum of electronic and thermal Enthalpies= -1137.060645
Sum of electronic and thermal Free Energies= -1137.112821

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 104.176 44.478 109.814

C,0,1.3808052492,-0.1790984205,1.2150657253
C,0,3.2485195488,-1.1046086776,-0.5984768334
C,0,2.6600428452,0.4238640053,1.1419762024
C,0,1.0813986765,-1.3063225731,0.4319121017
C,0,3.5902400313,-0.0471016994,0.2309442152
C,0,2.0014636881,-1.7434294623,-0.4902389748
H,0,0.6649692357,0.1701832907,1.9463477573
H,0,3.9581589183,-1.4563187812,-1.3349639493
H,0,2.8919539507,1.2578040922,1.7907612374
H,0,0.124883694,-1.7976488336,0.5427540226
H,0,4.562211449,0.4173184686,0.1530787729
H,0,1.7737778722,-2.5807993605,-1.1342095695
N,0,0.921870416,1.4081211505,-0.3438201047
O,0,1.2999043668,1.0488741651,-1.349674275
O,0,0.3454188767,2.1660555624,0.2810778143
S,0,-2.245054708,-0.0880996204,-0.0392357781
O,0,-2.5956427662,-1.5966039417,-0.2591598342
O,0,-1.7988912621,0.0159803287,1.3056628391
O,0,-3.6278408463,0.6344200468,-0.1015994545
O,0,-1.4174556668,0.364476163,-1.1158316087
H,0,-3.8800348189,0.8515530891,-1.0127155056
H,0,-2.6805347504,-1.8162769919,-1.2005068005
π-complex for the nitration of benzene / H2SO4 in water
scrf=(solvent=water)
m062x/6-311++G**
E(RM062X) = -1137.23415202

Zero-point correction= 0.155069 (Hartree/Particle)
Thermal correction to Energy= 0.170106
Thermal correction to Enthalpy= 0.171051
Thermal correction to Gibbs Free Energy= 0.110779
Sum of electronic and ZPE= -1137.079083
Sum of electronic and thermal Energies= -1137.064046
Sum of electronic and thermal Enthalpies= -1137.063101
Sum of electronic and thermal Free Energies= -1137.123373

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 106.743 51.966 126.852

C,0,-0.9484656687,-0.0958313958,1.415685958
C,0,-2.4985233005,0.9219691104,-0.6665822876
C,0,-2.1695753588,-0.6947296552,1.0962301636
C,0,-0.5104501523,1.01695238,0.6984043148
C,0,-2.9449086834,-0.182758343,0.0560612586
C,0,-1.281345557,1.5214935754,-0.346147518
H,0,-0.3459424069,-0.4857560768,2.2287996837
H,0,-3.0985052251,1.315955275,-1.4783130989
H,0,-2.5195391988,-1.5492474998,1.6643745114
H,0,0.425828332,1.4952381555,0.9615944067
H,0,-3.8936702599,-0.6448707343,-0.1893621263
H,0,-0.9358962077,2.3820712125,-0.9068075186
N,0,-0.2127135319,-1.9998584634,-0.8229670052
O,0,-0.5938534734,-1.3214462013,-1.6078150001
O,0,0.1556999359,-2.7231636999,-0.0702641559
S,0,2.775474817,-0.0625828872,0.087093629
O,0,2.7911920658,1.4877746247,-0.2261532251
O,0,2.6008747025,-0.1816026979,1.4982360877
O,0,4.2527268263,-0.5261252244,-0.2174217048
O,0,1.8760197432,-0.7113554716,-0.8399859564
H,0,4.4244555654,-0.6450780745,-1.1667535342
H,0,2.6511170367,1.6829520913,-1.1679068827

π-complex for the nitration of benzene / H2SO4 with eps=109
Scrf=(solvent=generic=read)
eps=109
epsinf=2.016
rsolv=2.5
m062x/6-311++G**
E(RM062X) = -1137.23458220

Zero-point correction= 0.155119 (Hartree/Particle)
Thermal correction to Energy= 0.170140
Thermal correction to Enthalpy= 0.171085
Thermal correction to Gibbs Free Energy= 0.110960
Sum of electronic and ZPE= -1137.079463
Sum of electronic and thermal Energies= -1137.064442
Sum of electronic and thermal Enthalpies= -1137.063498
Sum of electronic and thermal Free Energies= -1137.123622

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 106.765 51.962 126.543

C,0,-0.9495407485,-0.0982248932,1.4167261157
C,0,-2.496323829,0.9220697864,-0.6670537172

C,0,-2.1717932407,-0.6945188796,1.0969163102
C,0,-0.5084864255,1.0127317903,0.6986735394
C,0,-2.9454397792,-0.1813297013,0.0561186405
C,0,-1.2776613332,1.5186299609,-0.3466770122
H,0,-0.3480548955,-0.4893785751,2.2299728952
H,0,-3.0949533001,1.3168006123,-1.4793926484
H,0,-2.5236470391,-1.5483022815,1.664904813
H,0,0.4294069547,1.4882867817,0.9608188285
H,0,-3.8948843515,-0.6418544685,-0.189601185
H,0,-0.9293205909,2.3775322051,-0.9081277399
N,0,-0.2097875277,-1.9999551707,-0.8195094553
O,0,-0.5969115274,-1.3261797078,-1.6053247294
O,0,0.1650186105,-2.7190308474,-0.0659426744
S,0,2.7725626398,-0.0589612752,0.0854612185
O,0,2.7933954028,1.4926596087,-0.2245519727
O,0,2.5935365545,-0.1820676821,1.4955723955
O,0,4.2496720714,-0.5250306049,-0.2187218175
O,0,1.8744260969,-0.7027825209,-0.8459105766
H,0,4.4173338872,-0.649264124,-1.1683038917
H,0,2.6514523708,1.6881699872,-1.1660473365

Calculated Structures for Friedel-Craft Acylations

Acetylium Ion (CH3CO cation)
*B3LYP/6-31+G***
E(RB+HF-LYP) = -152.929757711

Zero-point correction= 0.044513 (Hartree/Particle)
Thermal correction to Energy= 0.048082
Thermal correction to Enthalpy= 0.049027
Thermal correction to Gibbs Free Energy= 0.020442
Sum of electronic and ZPE= -152.885245
Sum of electronic and thermal Energies= -152.881675
Sum of electronic and thermal Enthalpies= -152.880731
Sum of electronic and thermal Free Energies= -152.909316

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	30.172	10.368	60.162

C,0,0.0553626033,-0.0083676744,-0.2075902544
C,0,-0.313760406,0.0475818483,1.1751824648
O,0,0.3451467003,-0.052342177,-1.2927316642
H,0,-1.2780836393,-0.4666893252,1.3001054657
H,0,0.467719245,-0.4534086669,1.7653616382
H,0,-0.4004223923,1.1035503647,1.4708329473

*B3LYP/6-31+G**/PCM G03*
Done with Gaussian 03 defaults
E(RB+HF-LYP) = -153.020663268

Zero-point correction= 0.044271 (Hartree/Particle)
Thermal correction to Energy= 0.047847
Thermal correction to Enthalpy= 0.048791
Thermal correction to Gibbs Free Energy= 0.020197
Sum of electronic and ZPE= -152.976392
Sum of electronic and thermal Energies= -152.972817
Sum of electronic and thermal Enthalpies= -152.971873
Sum of electronic and thermal Free Energies= -153.000466

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 30.024 10.404 60.180

C,0,0.0535407511,-0.0081031881,-0.2006565859
C,0,-0.3146842661,0.0477167902,1.178954807
O,0,0.3431228139,-0.052042625,-1.2852795567
H,0,-1.2794592429,-0.4681576379,1.2961932035
H,0,0.4709200766,-0.454913589,1.7628128763
H,0,-0.3995691326,1.1061462499,1.4674492558

*B3LYP/6-31+G**/PCM G09*
E(RB3LYP) = -153.022378136

Zero-point correction= 0.044637 (Hartree/Particle)
Thermal correction to Energy= 0.048201
Thermal correction to Enthalpy= 0.049146
Thermal correction to Gibbs Free Energy= 0.020576
Sum of electronic and ZPE= -152.977741
Sum of electronic and thermal Energies= -152.974177
Sum of electronic and thermal Enthalpies= -152.973232
Sum of electronic and thermal Free Energies= -153.001802

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 30.247 10.355 60.130

C,0,0.0537985465,-0.0080721229,-0.1995389747
C,0,-0.3139811922,0.0474778653,1.1760616667
O,0,0.3427782188,-0.052016009,-1.2855207964
H,0,-1.2762107088,-0.4663866498,1.2946995983
H,0,0.4686916564,-0.4532337944,1.7599932066
H,0,-0.3991144097,1.1025550803,1.4654658968

*M062X/6-31+G***
E(RM062X) = -152.856781303

Zero-point correction= 0.045087 (Hartree/Particle)
Thermal correction to Energy= 0.048650
Thermal correction to Enthalpy= 0.049595
Thermal correction to Gibbs Free Energy= 0.021022

Sum of electronic and ZPE= -152.811694
Sum of electronic and thermal Energies= -152.808131
Sum of electronic and thermal Enthalpies= -152.807187
Sum of electronic and thermal Free Energies= -152.835760

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 30.529 10.342 60.137

C,0,0.0554757505,-0.008433189,-0.2080857802
C,0,-0.3151727149,0.0478943697,1.1805985051
O,0,0.3432870572,-0.0521380329,-1.2854373757
H,0,-1.2776075514,-0.4671064401,1.2959123709
H,0,0.4695037846,-0.4540149535,1.7612761228
H,0,-0.3995242149,1.1041226153,1.4668967545

*M062X/6-31+G**/PCM*
E(RM062X) = -152.949201993

Zero-point correction= 0.045155 (Hartree/Particle)
Thermal correction to Energy= 0.048718
Thermal correction to Enthalpy= 0.049662
Thermal correction to Gibbs Free Energy= 0.021097
Sum of electronic and ZPE= -152.904047
Sum of electronic and thermal Energies= -152.900484
Sum of electronic and thermal Enthalpies= -152.899540
Sum of electronic and thermal Free Energies= -152.928105

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 30.571 10.344 60.120

C,0,0.0527252999,-0.0083254112,-0.2003627217
C,0,-0.3156422775,0.0475010686,1.1816734686
O,0,0.3420091444,-0.0511643802,-1.2781605201
H,0,-1.2762596129,-0.4670145631,1.2913425364
H,0,0.4708387936,-0.4538115888,1.7559753015
H,0,-0.3977092365,1.1031392444,1.4606925327

*MP2/6-31+G**/PCM*
Done with Gaussian 09 defaults
EUMP2 = -0.15259448818986D+03

Zero-point correction= 0.045709 (Hartree/Particle)
Thermal correction to Energy= 0.049294
Thermal correction to Enthalpy= 0.050238
Thermal correction to Gibbs Free Energy= 0.021614
Sum of electronic and ZPE= -152.548779
Sum of electronic and thermal Energies= -152.545194
Sum of electronic and thermal Enthalpies= -152.544250

Sum of electronic and thermal Free Energies= -152.572874

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 30.932 10.311 60.244

6 0.209699 0.000239 -0.000145
6 -1.226211 -0.000007 0.000034
8 1.346650 -0.000072 0.000049
1 -1.557567 -0.565318 0.870395
1 -1.558575 1.036065 0.054214
1 -1.557984 -0.471562 -0.924334

Acetylium Ion BF4 Ion Pair
*B3LYP/6-31+G**/PCM G03*
Done with Gaussian 03 defaults
E(RB+HF-LYP) = -577.694687834

Zero-point correction= 0.059276 (Hartree/Particle)
Thermal correction to Energy= 0.068898
Thermal correction to Enthalpy= 0.069842
Thermal correction to Gibbs Free Energy= 0.022360
Sum of electronic and ZPE= -577.635411
Sum of electronic and thermal Energies= -577.625790
Sum of electronic and thermal Enthalpies= -577.624846
Sum of electronic and thermal Free Energies= -577.672328

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 43.234 30.721 99.935

C,0,1.8391993898,-1.2949030434,-0.6634012271
F,0,0.0001821695,0.5156369014,-0.6801919153
B,0,-0.9674428568,0.8187929185,0.3289263329
F,0,-0.6769417104,2.0635286767,0.8982248626
O,0,2.5916051808,-0.5915469555,-1.1171333027
C,0,0.8846944442,-2.1891165048,-0.0959981466
F,0,-2.2483560963,0.8121278847,-0.2357071206
F,0,-0.8738542315,-0.1994294582,1.3241160042
H,0,1.4246008062,-3.0094762434,0.3964295749
H,0,0.2687124854,-1.606451281,0.6109427107
H,0,0.2584253604,-2.5683201765,-0.9165177633

*B3LYP/6-31+G**/PCM G09*
E(RB3LYP) = -577.694658535

Zero-point correction= 0.059908 (Hartree/Particle)
Thermal correction to Energy= 0.069375
Thermal correction to Enthalpy= 0.070319
Thermal correction to Gibbs Free Energy= 0.023571

Sum of electronic and ZPE= -577.634750
Sum of electronic and thermal Energies= -577.625284
Sum of electronic and thermal Enthalpies= -577.624340
Sum of electronic and thermal Free Energies= -577.671088

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 43.533 30.586 98.389

C,0,1.7588896449,-1.2031816384,-0.605572027
F,0,-0.0081065573,0.409495278,-0.7113614467
B,0,-0.9465010409,0.8058566999,0.3106041213
F,0,-0.602111033,2.0778980746,0.7746994621
O,0,2.5715776789,-0.525791993,-0.9942747799
C,0,0.8651418375,-2.1939275259,-0.0994011785
F,0,-2.235254622,0.7931426296,-0.230249451
F,0,-0.8477288186,-0.1426650553,1.3630162148
H,0,1.4706270346,-3.0345552211,0.2592441994
H,0,0.2690984773,-1.7314765932,0.7008730959
H,0,0.2051923399,-2.5039519365,-0.9178882007

*M062X/6-31+G**/PCM*
E(RM062X) = -577.484795861

Zero-point correction= 0.061093 (Hartree/Particle)
Thermal correction to Energy= 0.070503
Thermal correction to Enthalpy= 0.071447
Thermal correction to Gibbs Free Energy= 0.025177
Sum of electronic and ZPE= -577.423702
Sum of electronic and thermal Energies= -577.414293
Sum of electronic and thermal Enthalpies= -577.413349
Sum of electronic and thermal Free Energies= -577.459619

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 44.241 30.331 97.384

C,0,1.6123113347,-1.0881148746,-0.1837941153
F,0,-0.2253378699,0.2662898538,-1.0300313957
B,0,-0.7812464633,0.7741240008,0.1818087229
F,0,-0.6832175154,2.1572542672,0.203456182
O,0,2.4147512612,-0.3093527155,-0.2081171437
C,0,0.7211585739,-2.2150655245,-0.1640083825
F,0,-2.1007506088,0.3505762609,0.2972746942
F,0,-0.0057700705,0.2113643971,1.2336167455
H,0,1.335914575,-3.1108482107,-0.0372716836
H,0,0.0319209082,-2.0664848484,0.6712576652
H,0,0.1810908749,-2.218899606,-1.114498289

*MP2/6-31+G**/PCM*

Done with Gaussian 09 defaults
EUMP2 = -0.57626345371082D+03

Zero-point correction= 0.060951 (Hartree/Particle)
Thermal correction to Energy= 0.070620
Thermal correction to Enthalpy= 0.071564
Thermal correction to Gibbs Free Energy= 0.024267
Sum of electronic and ZPE= -576.202503
Sum of electronic and thermal Energies= -576.192834
Sum of electronic and thermal Enthalpies= -576.191890
Sum of electronic and thermal Free Energies= -576.239187

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 44.315 30.652 99.545

6 -1.961663 -0.222493 -0.004452
9 0.275042 -0.001126 -1.123729
5 1.170293 0.007113 0.001157
9 2.013963 -1.111431 -0.053882
8 -2.003760 -1.359107 0.001548
6 -2.087320 1.211603 0.000312
9 1.903826 1.204916 0.008108
9 0.341803 -0.059436 1.169914
1 -3.135772 1.442242 0.184256
1 -1.444343 1.591781 0.790783
1 -1.759078 1.572306 -0.972067

Veratrole (**5**), Conformation 1
B3LYP/6-31+G**
E(RB+HF-LYP) = -461.320507331

Zero-point correction= 0.165542 (Hartree/Particle)
Thermal correction to Energy= 0.174995
Thermal correction to Enthalpy= 0.175939
Thermal correction to Gibbs Free Energy= 0.130970
Sum of electronic and ZPE= -461.154965
Sum of electronic and thermal Energies= -461.145512
Sum of electronic and thermal Enthalpies= -461.144568
Sum of electronic and thermal Free Energies= -461.189537

E CV S
KCAL/MOL CAL/MOL-K CAL/MOL-K
TOTAL 109.811 35.570 94.645

C,0,-1.2447254035,0.1511358371,-1.2450793797
C,0,-2.2085550363,0.8174062617,-0.4718131895
C,0,-1.9432719393,1.121396925,0.8570822728
C,0,-0.7114136876,0.7622589832,1.4266114291
C,0,0.2536396135,0.1001300771,0.6682018576

C,0,-0.0175094996,-0.2105447432,-0.6900744952
H,0,-2.6814062593,1.6363573121,1.4641415774
O,0,1.4770687055,-0.2894140993,1.1298803482
C,0,1.8066359784,-0.0060605328,2.4819261341
O,0,0.9804875681,-0.8584989272,-1.3578651267
C,0,0.7681957088,-1.1959663669,-2.720933638
H,0,-1.4620674076,-0.0811360525,-2.2808135824
H,0,-3.1577969061,1.0904486342,-0.9222976374
H,0,-0.5148918859,1.0042906725,2.4642723922
H,0,2.8131326555,-0.3997018525,2.6300553086
H,0,1.8062799875,1.0739720985,2.678428868
H,0,1.1165635091,-0.5020234004,3.1768380723
H,0,1.6800541581,-1.6980245462,-3.0470998552
H,0,-0.0840354228,-1.877811503,-2.8387617168
H,0,0.6057429765,-0.301605798,-3.3364111454

*B3LYP/6-31+G**/PCM G03*
Done with Gaussian 03 defaults
E(RB+HF-LYP) = -461.328204758

Zero-point correction= 0.164964 (Hartree/Particle)
Thermal correction to Energy= 0.174406
Thermal correction to Enthalpy= 0.175350
Thermal correction to Gibbs Free Energy= 0.130466
Sum of electronic and ZPE= -461.163240
Sum of electronic and thermal Energies= -461.153799
Sum of electronic and thermal Enthalpies= -461.152855
Sum of electronic and thermal Free Energies= -461.197738

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.441 35.681 94.466

C,0,-1.2429954366,0.1496965187,-1.2466042476
C,0,-2.2068186632,0.8162677423,-0.4726111231
C,0,-1.9410144657,1.1207264339,0.8577943705
C,0,-0.7087324675,0.7616213726,1.4277946875
C,0,0.2563902767,0.0989207659,0.6679236863
C,0,-0.0149921709,-0.2118385696,-0.6904271277
H,0,-2.6799524926,1.6368044966,1.4670214711
O,0,1.481932538,-0.2898641676,1.1346947017
C,0,1.802540065,-0.0000590243,2.495557226
O,0,0.9827620741,-0.8613202054,-1.3635544919
C,0,0.7591898483,-1.1958967097,-2.7333544042
H,0,-1.4647311863,-0.0809709547,-2.2829634409
H,0,-3.1578153675,1.0894565663,-0.9248279227
H,0,-0.5160334116,1.0058453543,2.4668386613
H,0,2.8088256158,-0.3912536266,2.6511137629
H,0,1.7967036831,1.0802593011,2.6843462558
H,0,1.106681114,-0.4964352362,3.1826921906

H,0,1.6681192093,-1.6988145537,-3.0661685471
H,0,-0.095443775,-1.8744209859,-2.8429279145
H,0,0.594687798,-0.2976265552,-3.3406846012

*B3LYP/6-31+G**/PCM G09*
E(RB3LYP) = -461.327202036

Zero-point correction= 0.165378 (Hartree/Particle)
Thermal correction to Energy= 0.174891
Thermal correction to Enthalpy= 0.175835
Thermal correction to Gibbs Free Energy= 0.130688
Sum of electronic and ZPE= -461.161825
Sum of electronic and thermal Energies= -461.152311
Sum of electronic and thermal Enthalpies= -461.151367
Sum of electronic and thermal Free Energies= -461.196514

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.746 35.712 95.020

C,0,-1.2464520815,0.1513933329,-1.2466815607
C,0,-2.2099964198,0.8178368033,-0.4723935253
C,0,-1.9444306686,1.1221538638,0.8579693336
C,0,-0.7124252222,0.7633558266,1.4285088395
C,0,0.2519315382,0.101043791,0.6683698522
C,0,-0.0192030701,-0.2096950731,-0.6899328747
H,0,-2.6822173731,1.6369904357,1.4652207677
O,0,1.4767885779,-0.2884839658,1.1317424184
C,0,1.8046728034,-0.0022522751,2.4914330669
O,0,0.9794233303,-0.8584745855,-1.3596523167
C,0,0.7626080305,-1.1963412531,-2.7296783075
H,0,-1.463547123,-0.080954141,-2.2822124814
H,0,-3.1589788173,1.0906649875,-0.9231015776
H,0,-0.5157231385,1.0052272055,2.4659352808
H,0,2.8104732835,-0.3950125187,2.6414746016
H,0,1.8016577713,1.0771698859,2.6823726468
H,0,1.1118491428,-0.499018082,3.1805174246
H,0,1.6730690445,-1.6982936822,-3.0575699014
H,0,-0.0899574,-1.8762542846,-2.8413953346
H,0,0.5997605771,-0.2999583082,-3.3392731597

B3LYP/6-31G/PCM in acetic acid*
Done in Gaussian 03
E(RB+HF-LYP) = -461.293930461

Zero-point correction= 0.166066 (Hartree/Particle)
Thermal correction to Energy= 0.175465
Thermal correction to Enthalpy= 0.176409
Thermal correction to Gibbs Free Energy= 0.131580
Sum of electronic and ZPE= -461.127865

Sum of electronic and thermal Energies= -461.118466
Sum of electronic and thermal Enthalpies= -461.117522
Sum of electronic and thermal Free Energies= -461.162351

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 110.106 35.456 94.351

C,0,0.0414432697,-0.0314277499,0.0476991802
C,0,0.1046549375,-0.0795259015,1.4650292242
C,0,1.3471146534,-0.0780501377,2.0973364407
C,0,2.5289388599,-0.0295375751,1.3430370549
C,0,2.4671095861,0.0175360625,-0.0432587819
C,0,1.2227540985,0.0165401145,-0.6910316749
O,0,-1.1006964682,-0.1245731124,2.1070012814
H,0,1.409108154,-0.1144583018,3.17987256
H,0,3.4885530188,-0.0292415703,1.8554579265
H,0,3.3773562445,0.0553646545,-0.6377791714
H,0,1.1881321031,0.0534831147,-1.7747711334
O,0,-1.2163444926,-0.0367088822,-0.4861175001
C,0,-1.332641755,0.0113984574,-1.9027364133
H,0,-2.4036210521,-0.0009143034,-2.1142080355
H,0,-0.8914156285,0.9293971346,-2.3123589028
H,0,-0.8583407795,-0.8583392735,-2.3758155181
C,0,-1.09034842,-0.1740285803,3.5283099453
H,0,-2.1382891433,-0.2046951852,3.8328570449
H,0,-0.5779879631,-1.0723925923,3.8965773586
H,0,-0.6121532234,0.7153616274,3.9590301146

*M062X/6-31+G***
E(RM062X) = -461.112666680

Zero-point correction= 0.167580 (Hartree/Particle)
Thermal correction to Energy= 0.176933
Thermal correction to Enthalpy= 0.177877
Thermal correction to Gibbs Free Energy= 0.132834
Sum of electronic and ZPE= -460.945087
Sum of electronic and thermal Energies= -460.935734
Sum of electronic and thermal Enthalpies= -460.934790
Sum of electronic and thermal Free Energies= -460.979833

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 111.027 35.013 94.801

C,0,-1.2322082754,0.1460009287,-1.2441277015
C,0,-2.19339876,0.8110766955,-0.4707837178
C,0,-1.9291027378,1.1139304702,0.8533476295
C,0,-0.6997676683,0.7561183854,1.4234174719
C,0,0.2596299667,0.0967405947,0.665619825

C,0,-0.0106940442,-0.21302049,-0.6887119089
H,0,-2.6671560537,1.6284981543,1.4594563806
O,0,1.4775669922,-0.292629843,1.1200632473
C,0,1.7905307851,-0.0043140502,2.4653615147
O,0,0.984830196,-0.8572527149,-1.3485568096
C,0,0.7591555361,-1.1861273848,-2.70200128
H,0,-1.4486862332,-0.0866342917,-2.2798847293
H,0,-3.1421667772,1.0841885496,-0.9203608261
H,0,-0.5024170001,0.9976859995,2.4609492948
H,0,2.7953411682,-0.392228368,2.6292376421
H,0,1.7809300106,1.076499281,2.6530795279
H,0,1.0915116355,-0.4989103873,3.1510978085
H,0,1.6632014858,-1.6894918275,-3.0430320452
H,0,-0.098151754,-1.8621281027,-2.8094027529
H,0,0.591279366,-0.2866480595,-3.3071806156

*M062X/6-31+G**/PCM*
E(RM062X) = -461.119768843

Zero-point correction= 0.167358 (Hartree/Particle)
Thermal correction to Energy= 0.176766
Thermal correction to Enthalpy= 0.177710
Thermal correction to Gibbs Free Energy= 0.132486
Sum of electronic and ZPE= -460.952411
Sum of electronic and thermal Energies= -460.943003
Sum of electronic and thermal Enthalpies= -460.942058
Sum of electronic and thermal Free Energies= -460.987283

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 110.923 35.139 95.183

C,0,-1.2316529684,0.1452464488,-1.2458716893
C,0,-2.1927001734,0.8105444373,-0.4715014607
C,0,-1.9281531641,1.1136803105,0.8539153781
C,0,-0.6985617841,0.7560986821,1.4249870126
C,0,0.2603402541,0.0964864799,0.665632657
C,0,-0.0100143878,-0.2133045931,-0.6888791021
H,0,-2.6659548432,1.6282579919,1.4605066676
O,0,1.4795312069,-0.2929868207,1.1213949696
C,0,1.7914964947,-0.0022458499,2.4732860329
O,0,0.9862030476,-0.8582772666,-1.3502386096
C,0,0.7569777775,-1.1876653438,-2.7098052169
H,0,-1.4483530648,-0.0872730653,-2.2816086181
H,0,-3.1414079097,1.0834517685,-0.9215789206
H,0,-0.5014426022,0.9977613866,2.4625410628
H,0,2.7957448561,-0.3892570165,2.639236064
H,0,1.7797784926,1.0779583729,2.6565465519
H,0,1.09042383,-0.4973498603,3.1544117036
H,0,1.659658764,-1.6910585805,-3.0527251977

H,0,-0.1005186248,-1.8620090503,-2.812389292
H,0,0.5888326373,-0.2867048921,-3.3102720375

*MP2/6-31+G**/PCM*
EUMP2 = -0.45994349301178D+03

Zero-point correction= 0.165629 (Hartree/Particle)
Thermal correction to Energy= 0.174522
Thermal correction to Enthalpy= 0.175466
Thermal correction to Gibbs Free Energy= 0.131518
Sum of electronic and ZPE= -459.777864
Sum of electronic and thermal Energies= -459.768971
Sum of electronic and thermal Enthalpies= -459.768027
Sum of electronic and thermal Free Energies= -459.811975

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.514 33.570 92.498

1 3.124881 -0.919406 0.893493
6 1.401094 1.076789 -0.000114
6 0.695885 2.291282 -0.000042
6 -0.695611 2.291364 0.000072
6 -1.400980 1.076959 0.000088
6 -0.708648 -0.135867 0.000087
6 0.708615 -0.135943 -0.000154
1 -1.245407 3.224192 0.000112
8 -1.294127 -1.374887 0.000161
6 -2.727399 -1.402531 -0.000097
8 1.293974 -1.375014 -0.000281
6 2.727242 -1.402733 0.000221
1 2.481632 1.090753 -0.000226
1 1.245798 3.224042 -0.000043
1 -2.481514 1.091065 0.000200
1 -2.992401 -2.454707 -0.000123
1 -3.125521 -0.919164 0.892937
1 -3.125172 -0.919193 -0.893303
1 2.992193 -2.454922 0.000294
1 3.125546 -0.919389 -0.892746
1 3.124881 -0.919406 0.893493

Veratrole (**5**), Conformation 2
*B3LYP/6-31+G***
E(RB+HF-LYP) = -461.318630183

Zero-point correction= 0.165205 (Hartree/Particle)
Thermal correction to Energy= 0.174829
Thermal correction to Enthalpy= 0.175773
Thermal correction to Gibbs Free Energy= 0.130356
Sum of electronic and ZPE= -461.153425

Sum of electronic and thermal Energies= -461.143801
Sum of electronic and thermal Enthalpies= -461.142857
Sum of electronic and thermal Free Energies= -461.188274

E CV S
KCAL/MOL CAL/MOL-K CAL/MOL-K
TOTAL 109.707 35.715 95.588

C,0,-0.0057844965,-0.0529689047,-0.8787702081
C,0,-1.2377006217,0.1258110946,-1.5039377471
C,0,-2.3574524623,0.5489003414,-0.7788320746
C,0,-2.2366660743,0.7888017025,0.5880961383
C,0,-1.0042050663,0.6183121985,1.2312210997
C,0,0.1194235837,0.2056177047,0.5064316531
O,0,1.3668827541,0.0374751997,1.0414860454
C,0,1.5590817302,0.3356580999,2.4186376847
O,0,1.0814350753,-0.4000024543,-1.6463185956
C,0,1.6314118868,-1.7021557878,-1.4109765542
H,0,-3.0958882527,1.1143375339,1.1669489269
H,0,-1.2957534678,-0.0644127234,-2.5712215316
H,0,-3.3098838008,0.6857643689,-1.2813334212
H,0,-0.9268646574,0.8195802598,2.29318568
H,0,2.6165176635,0.1551523596,2.6161960999
H,0,1.3223902551,1.3845612618,2.636152645
H,0,0.9521232008,-0.3166457625,3.0592222579
H,0,2.4499838476,-1.8155591596,-2.124355601
H,0,2.0159584378,-1.7934655775,-0.3909859838
H,0,0.876223261,-2.4769532183,-1.5963686213

*M062X/6-31+G***
E(RM062X) = -461.111149270

Zero-point correction= 0.167589 (Hartree/Particle)
Thermal correction to Energy= 0.176948
Thermal correction to Enthalpy= 0.177892
Thermal correction to Gibbs Free Energy= 0.133164
Sum of electronic and ZPE= -460.943560
Sum of electronic and thermal Energies= -460.934202
Sum of electronic and thermal Enthalpies= -460.933257
Sum of electronic and thermal Free Energies= -460.977985

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 111.036 35.034 94.137

C,0,-0.1946817647,-0.0003743129,-0.7822087912
C,0,-0.1704062655,-0.012282171,0.6270791099
C,0,1.0439823971,-0.0258871003,1.2972346863
C,0,2.2486691203,-0.0316973691,0.589843537
C,0,2.2242963246,-0.0298479291,-0.7984262692

C,0,1.0080669914,-0.015064806,-1.4873830284
O,0,-1.3335028316,0.0505306786,1.3453721496
H,0,1.0212740216,-0.020279868,2.3824880612
H,0,3.1923674354,-0.0372940065,1.1247476401
H,0,3.1511339361,-0.034702667,-1.3629442872
H,0,1.0109009699,-0.0052815022,-2.570842456
O,0,-1.4271601636,0.035028362,-1.3566628848
C,0,-1.4884249119,0.0839619458,-2.7672739731
H,0,-2.547208219,0.1214300194,-3.0211686328
H,0,-0.9884619479,0.9802597118,-3.1528184045
H,0,-1.0354013186,-0.8087081655,-3.2152804461
C,0,-2.1211189923,-1.1345757955,1.3005826653
H,0,-2.9922803491,-0.9465910978,1.9289526911
H,0,-2.4432635334,-1.3535833658,0.2787477988
H,0,-1.5538148986,-1.982278561,1.7037758339

*M062X/6-31+G**/PCM*
E(RM062X) = -461.117197677

Zero-point correction= 0.167164 (Hartree/Particle)
Thermal correction to Energy= 0.176596
Thermal correction to Enthalpy= 0.177541
Thermal correction to Gibbs Free Energy= 0.132520
Sum of electronic and ZPE= -460.950034
Sum of electronic and thermal Energies= -460.940601
Sum of electronic and thermal Enthalpies= -460.939657
Sum of electronic and thermal Free Energies= -460.984678

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 110.816 35.170 94.754

C,0,-0.2022980778,0.0327222526,-0.7939869841
C,0,-0.1830480217,0.0090059286,0.6151876051
C,0,1.0252716559,-0.0344727594,1.2952761572
C,0,2.2341488411,-0.0552046614,0.5935442859
C,0,2.2161392391,-0.0376855345,-0.7959584782
C,0,1.0046163912,0.0051974061,-1.4935697015
O,0,-1.3591352612,0.0766839936,1.3187746812
H,0,1.0001283061,-0.0456778797,2.3808073832
H,0,3.1749863783,-0.0847449573,1.1327416462
H,0,3.1460622606,-0.0531947743,-1.3553412683
H,0,1.0139013485,0.0245614564,-2.5768497489
O,0,-1.4311988074,0.0904567637,-1.3695859796
C,0,-1.4917763453,0.0975177857,-2.787344953
H,0,-2.5498992802,0.1368003201,-3.0412529878
H,0,-0.9833887934,0.9764412007,-3.1978393049
H,0,-1.0467933595,-0.813044547,-3.2030208635
C,0,-2.0950793903,-1.1475116162,1.325910118
H,0,-3.0046214123,-0.9598540551,1.8967408524

H,0,-2.3531921315,-1.4496006201,0.306709862
H,0,-1.5098575402,-1.9356337025,1.8128726785

Veratrole (**5**), Conformation 3
*B3LYP/6-31+G***
E(RB+HF-LYP) = -461.316374852

Zero-point correction= 0.164615 (Hartree/Particle)
Thermal correction to Energy= 0.174511
Thermal correction to Enthalpy= 0.175455
Thermal correction to Gibbs Free Energy= 0.129109
Sum of electronic and ZPE= -461.151760
Sum of electronic and thermal Energies= -461.141864
Sum of electronic and thermal Enthalpies= -461.140920
Sum of electronic and thermal Free Energies= -461.187266

E CV S
KCAL/MOL CAL/MOL-K CAL/MOL-K
TOTAL 109.507 35.929 97.543

C,0,0.1263244798,0.1966528914,0.6650300522
C,0,-0.1781796908,-0.1780020626,-0.6585670977
C,0,-1.4529876788,0.0732622857,-1.1714639068
C,0,-2.4334236647,0.6679007657,-0.3726642108
C,0,-2.1411375571,1.0094594559,0.9501334846
C,0,-0.8626322462,0.7758342256,1.4636779009
O,0,0.7760930374,-0.7421245655,-1.4792452177
C,0,1.1271102866,-2.0968828393,-1.1574643298
O,0,1.3709053856,-0.0453518199,1.2079829944
C,0,2.4228572447,0.7955646511,0.7096336222
H,0,-1.6574104664,-0.2089340507,-2.1998085054
H,0,-3.4216390213,0.8555724106,-0.7817108945
H,0,-2.9007864024,1.4627750872,1.5798623992
H,0,-0.6079547829,1.0397262066,2.4856459688
H,0,1.8932385099,-2.3905235711,-1.8775551847
H,0,1.5233350752,-2.1709618119,-0.1397505813
H,0,0.2544701407,-2.7531495027,-1.2644231689
H,0,3.333885517,0.4747457909,1.218355551
H,0,2.5398436401,0.6818668723,-0.372780974
H,0,2.2194433644,1.8459574105,0.9523700868

Ion-Pair Transition Structure (Structure **16**‡)
*B3LYP/6-31+G**/PCM G03*
Done with Gaussian 03 defaults.
E(RB+HF-LYP) = -1039.02462372

Zero-point correction= 0.225515 (Hartree/Particle)
Thermal correction to Energy= 0.245744
Thermal correction to Enthalpy= 0.246688
Thermal correction to Gibbs Free Energy= 0.173839

Sum of electronic and ZPE= -1038.799109
Sum of electronic and thermal Energies= -1038.778880
Sum of electronic and thermal Enthalpies= -1038.777936
Sum of electronic and thermal Free Energies= -1038.850785

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	154.206	70.251	153.324

6	0.449791	-0.879652	1.593664
6	1.537370	-1.720464	1.317659
6	-0.438269	-1.860132	-0.730858
9	-2.442127	-0.140938	-1.160868
5	-3.297306	0.415211	-0.167348
9	-2.844686	1.697724	0.180751
8	0.207357	-1.334145	-1.503885
6	-1.439760	-2.718537	-0.141344
9	-4.611782	0.474229	-0.659229
9	-3.251645	-0.434798	0.973868
6	2.624750	-1.238672	0.578745
6	0.460053	0.459502	1.158131
1	1.554493	-2.742153	1.693302
1	-0.368176	-1.225516	2.222230
1	-0.942408	-3.489665	0.455500
1	-2.099977	-2.100988	0.480050
1	-2.004720	-3.160597	-0.974358
6	2.629193	0.079184	0.112787
1	3.458120	-1.900225	0.369217
8	3.623498	0.634744	-0.617156
6	1.528787	0.943529	0.410134
1	-0.382764	1.097919	1.393245
8	1.624719	2.203557	-0.079341
6	4.761179	-0.169856	-0.949485
1	5.415055	0.478136	-1.533244
1	5.283064	-0.503479	-0.045736
1	4.466626	-1.036196	-1.552341
6	0.545358	3.112284	0.183780
1	0.817341	4.038707	-0.322386
1	-0.399259	2.729925	-0.215427
1	0.445992	3.295736	1.259779

*B3LYP/6-31+G**/PCM G09*
E(RB3LYP) = -1039.02369877

Zero-point correction= 0.226462 (Hartree/Particle)
Thermal correction to Energy= 0.246644
Thermal correction to Enthalpy= 0.247588
Thermal correction to Gibbs Free Energy= 0.174647
Sum of electronic and ZPE= -1038.797236
Sum of electronic and thermal Energies= -1038.777055

Sum of electronic and thermal Enthalpies= -1038.776111
Sum of electronic and thermal Free Energies= -1038.849052

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 154.771 70.079 153.518

C,0,0.1047931626,-0.5735451233,1.4836934888
C,0,1.0718833356,-1.5901184803,1.4666547709
C,0,-0.5436613264,-1.7999471673,-0.7553847462
F,0,-2.5049041996,0.0377953004,-0.9906418215
B,0,-3.3924963905,0.4709981757,0.0365325423
F,0,-2.8998085787,1.6549913681,0.6123909985
O,0,0.1280937054,-1.2898080899,-1.5206287729
C,0,-1.5629148309,-2.6926226954,-0.247470179
F,0,-4.6705300149,0.678506134,-0.502180855
F,0,-3.4469384353,-0.5505175728,1.0269915837
C,0,2.3242641501,-1.3597084412,0.8812074342
C,0,0.3960551235,0.6894982128,0.9382466718
H,0,0.8724800237,-2.5462798416,1.9403590901
H,0,-0.8474367143,-0.7250944926,1.9807972348
H,0,-1.0797618687,-3.4819790397,0.3340686246
H,0,-2.2602015827,-2.1195042724,0.3734509141
H,0,-2.0796403406,-3.1084971785,-1.1213794799
C,0,2.6107922551,-0.120018993,0.3085947639
H,0,3.0638687581,-2.1504442276,0.8727900869
O,0,3.7767474877,0.20141627,-0.2941020283
C,0,1.6305074046,0.9238280344,0.3424775385
H,0,-0.3655045645,1.4584515028,0.9593712445
O,0,2.0089021313,2.0911359833,-0.2283641962
C,0,4.8105729756,-0.7883396519,-0.3656211892
H,0,5.6367919842,-0.3085874859,-0.8888959296
H,0,5.1335650752,-1.0899180672,0.6361710125
H,0,4.4747647622,-1.6642370253,-0.9306167213
C,0,1.0777822657,3.1816922371,-0.2301537193
H,0,1.5905603724,4.0004957905,-0.7336454151
H,0,0.1687597846,2.9192989043,-0.7805752729
H,0,0.8221080897,3.4783779327,0.7924203263

*M062X/6-31+G**/PCM*
E(RM062X) = -1038.61317358

Zero-point correction= 0.230576 (Hartree/Particle)
Thermal correction to Energy= 0.249890
Thermal correction to Enthalpy= 0.250834
Thermal correction to Gibbs Free Energy= 0.181976
Sum of electronic and ZPE= -1038.382598
Sum of electronic and thermal Energies= -1038.363284
Sum of electronic and thermal Enthalpies= -1038.362339
Sum of electronic and thermal Free Energies= -1038.431198

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 156.808 68.595 144.924

C,0,0.3525835064,-0.9670443228,1.3705583553
C,0,1.5154208539,-1.7502228962,1.2666456071
C,0,-0.1909685353,-1.8462850451,-0.6478011802
F,0,-2.0724429142,-0.1219453904,-0.924534389
B,0,-2.9194455244,0.3374668326,0.1149781019
F,0,-2.5914826993,1.6631752935,0.4267862969
O,0,0.4362996483,-1.3779482043,-1.4772538144
C,0,-1.2313617754,-2.8011162225,-0.2554386579
F,0,-4.2506103607,0.2378686589,-0.2834825139
F,0,-2.691926024,-0.4780510077,1.2480501473
C,0,2.6480410007,-1.2379803486,0.6411717201
C,0,0.3582467616,0.379808522,0.9421883609
H,0,1.5313604576,-2.7598953306,1.6650855317
H,0,-0.5044256858,-1.3249885467,1.9310728628
H,0,-0.753415401,-3.6056628687,0.308112812
H,0,-1.9633342441,-2.2806661146,0.3646924164
H,0,-1.6812854267,-3.1740846373,-1.179017514
C,0,2.6281219859,0.062785577,0.1351216849
H,0,3.5318430312,-1.8545467995,0.5386225461
O,0,3.6452408614,0.6429059744,-0.5078385938
C,0,1.4685036368,0.8855884272,0.297438266
H,0,-0.5364828909,0.9777842917,1.0689471955
O,0,1.5705854636,2.1244597108,-0.216476424
C,0,4.8368942994,-0.1127959017,-0.7096449785
H,0,5.5136707591,0.5458025431,-1.2497443461
H,0,5.2811610304,-0.3960911948,0.2489243109
H,0,4.6288701402,-1.0047551221,-1.307896474
C,0,0.4187004208,2.9598067994,-0.1207800202
H,0,0.6806963278,3.8829458054,-0.6342975237
H,0,-0.4438725883,2.4878482123,-0.6003212432
H,0,0.1826208851,3.1716183049,0.9273224573

Intermediate σ-Cation – (Structure **12**)
*B3LYP/6-31+G***
E(RB+HF-LYP) = -614.302586611

Zero-point correction= 0.213664 (Hartree/Particle)
Thermal correction to Energy= 0.227291
Thermal correction to Enthalpy= 0.228236
Thermal correction to Gibbs Free Energy= 0.172769
Sum of electronic and ZPE= -614.088923
Sum of electronic and thermal Energies= -614.075295
Sum of electronic and thermal Enthalpies= -614.074351
Sum of electronic and thermal Free Energies= -614.129818

E CV S
KCAL/MOL CAL/MOL-K CAL/MOL-K
TOTAL 142.627 49.781 116.739

6 -0.861692 0.765043 0.163752
6 -1.354061 -0.598278 0.046851
6 -0.481309 -1.711289 0.246313
6 0.831794 -1.504662 0.541930
6 1.406867 -0.153315 0.647188
6 0.460011 0.962799 0.440667
8 -2.615674 -0.705786 -0.247938
6 -3.271756 -1.992835 -0.418847
6 2.761016 0.059247 -0.211519
6 3.712011 -1.105720 -0.291108
8 -1.794612 1.701343 -0.043633
6 -1.407921 3.086368 0.020921
8 2.963416 1.139450 -0.695471
1 -0.874237 -2.717857 0.173927
1 1.475045 -2.360253 0.722501
1 0.872541 1.963512 0.476099
1 -2.319618 3.646768 -0.177105
1 -1.028278 3.332518 1.018040
1 -0.657119 3.311862 -0.743220
1 -4.301649 -1.742953 -0.662836
1 -2.807182 -2.539953 -1.241858
1 -3.228369 -2.557652 0.514800
1 3.318913 -1.855607 -0.988135
1 4.674228 -0.750492 -0.662257
1 3.843544 -1.587536 0.683473
1 1.837384 -0.066559 1.666018

*B3LYP/6-31+G**/PCM G03*
EDone with Gaussian 03 defaults.
(RB+HF-LYP) = -614.371445010

Zero-point correction= 0.212884 (Hartree/Particle)
Thermal correction to Energy= 0.226386
Thermal correction to Enthalpy= 0.227330
Thermal correction to Gibbs Free Energy= 0.172484
Sum of electronic and ZPE= -614.158561
Sum of electronic and thermal Energies= -614.145059
Sum of electronic and thermal Enthalpies= -614.144115
Sum of electronic and thermal Free Energies= -614.198961

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 142.059 49.619 115.433

C,0,1.1417392803,0.1776803102,0.1373835765
C,0,0.8019501716,-0.1752270483,-1.2304506516

C,0,-0.5372100565,-0.0603977297,-1.7063888237
C,0,-1.5218895323,0.3610308052,-0.8672901936
C,0,-1.2565018412,0.710559997,0.5410884404
C,0,0.1517992104,0.5846544311,0.9790954937
O,0,1.7993594515,-0.5879176288,-1.9578810218
C,0,1.6217367962,-0.9922498927,-3.3443635687
C,0,-2.2655321711,0.0540580403,1.5746427315
C,0,-3.7028788898,-0.0788788114,1.1483589165
O,0,2.4482247496,0.0400504375,0.4305944149
C,0,2.8750855188,0.3460026881,1.7677647318
O,0,-1.8606855735,-0.2751072929,2.6658968651
H,0,-0.7733631011,-0.2985485545,-2.7383252366
H,0,-2.5307036222,0.4729181724,-1.2592046716
H,0,0.3598798966,0.8259620152,2.0153876227
H,0,3.950054812,0.169987878,1.7750728978
H,0,2.6668280746,1.3941298808,2.0091592516
H,0,2.3837028992,-0.3144563816,2.490527939
H,0,2.6159267182,-1.2899468939,-3.6712849667
H,0,0.930783599,-1.8366164603,-3.397180006
H,0,1.2622440129,-0.14464543,-3.9322739425
H,0,-3.7963646807,-0.9043999013,0.4314779322
H,0,-4.3169805759,-0.2970104674,2.0234211048
H,0,-4.060285629,0.8314589372,0.654760926
H,0,-1.5452005177,1.7872698998,0.6461962382

*B3LYP/6-31+G**/PCM G09*
E(RB3LYP) = -614.370062183

Zero-point correction= 0.214061 (Hartree/Particle)
Thermal correction to Energy= 0.227510
Thermal correction to Enthalpy= 0.228454
Thermal correction to Gibbs Free Energy= 0.173704
Sum of electronic and ZPE= -614.156001
Sum of electronic and thermal Energies= -614.142553
Sum of electronic and thermal Enthalpies= -614.141608
Sum of electronic and thermal Free Energies= -614.196358

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 142.764 49.507 115.231

C,0,1.143770722,0.172247104,0.135671677
C,0,0.8048774222,-0.1762556994,-1.2336437175
C,0,-0.5384757401,-0.0775534848,-1.7042889658
C,0,-1.5238595608,0.3380699655,-0.8649963292
C,0,-1.2563227732,0.7003754817,0.5407005645
C,0,0.1511011788,0.567934008,0.9793502343
O,0,1.8028992089,-0.5733309685,-1.9660882844
C,0,1.6277063984,-0.9759021067,-3.3551034275
C,0,-2.2756883427,0.0734930401,1.5858144121

C,0,-3.709310181,-0.0654248567,1.1508937886
O,0,2.4490600085,0.037291526,0.4302320098
C,0,2.8753169181,0.3421132664,1.7693863677
O,0,-1.8770354667,-0.2214866815,2.6886194131
H,0,-0.7661019688,-0.3250999241,-2.7328326648
H,0,-2.5354325148,0.4358800334,-1.2439943677
H,0,0.3598725132,0.7904867923,2.0176156612
H,0,3.9501355594,0.1702614852,1.7753449401
H,0,2.6632048297,1.3883051758,2.0117045652
H,0,2.3873246845,-0.3220870135,2.4894013492
H,0,2.626711838,-1.2453195068,-3.6878763298
H,0,0.9606024726,-1.8375683721,-3.4057760468
H,0,1.2440576144,-0.136196631,-3.9363878042
H,0,-3.7993928925,-0.9019017077,0.4477739857
H,0,-4.3295129159,-0.2677835651,2.0245758376
H,0,-4.0626113592,0.8366460398,0.6414213978
H,0,-1.5311786533,1.7731675997,0.628667734

*M062X/6-31+G***
E(RM062X) = -614.023607928

Zero-point correction= 0.216620 (Hartree/Particle)
Thermal correction to Energy= 0.229991
Thermal correction to Enthalpy= 0.230936
Thermal correction to Gibbs Free Energy= 0.176539
Sum of electronic and ZPE= -613.806988
Sum of electronic and thermal Energies= -613.793617
Sum of electronic and thermal Enthalpies= -613.792672
Sum of electronic and thermal Free Energies= -613.847069

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 144.322 49.219 114.488

C,0,-0.5014126604,0.9017996432,-0.8057724049
C,0,0.7484196645,0.7343646442,-0.3012592249
C,0,1.2364979475,-0.6202668848,-0.0903464465
C,0,0.4977403233,-1.7542569916,-0.543737254
C,0,-0.7467705065,-1.5687902814,-1.0518797335
C,0,-1.3888164929,-0.255197364,-1.0070453912
O,0,1.6295793253,1.6784258811,0.0266820317
C,0,1.234373561,3.0368434951,-0.1515207338
O,0,2.3904278383,-0.6948127772,0.4807082704
C,0,3.0135236888,-1.9658214825,0.7615849154
C,0,-2.2693998109,-0.3575628397,0.4068831474
O,0,-1.6818090683,-0.4865318976,1.4307998306
C,0,-3.7505583066,-0.2580967106,0.2093085729
H,0,-2.1215110124,-0.1066231167,-1.8022967454
H,0,0.9365279899,-2.7424360014,-0.4872334498
H,0,-1.3252075947,-2.4202065543,-1.4008756556

H,0,-0.9111380839,1.8934064086,-0.9631242671
H,0,2.0860615143,3.6344158827,0.1646423261
H,0,1.0120398661,3.2347315952,-1.2052283389
H,0,0.3655958086,3.2661685072,0.4741221981
H,0,3.9326718623,-1.7157650167,1.284183938
H,0,2.359425703,-2.5618510657,1.4007596556
H,0,3.2374993458,-2.4800876729,-0.1748713862
H,0,-4.084050295,-1.0552378291,-0.4628927305
H,0,-4.2528072597,-0.3371425852,1.1730415365
H,0,-3.9899926654,0.6973647688,-0.2684788159

*M062X/6-31+G**/PCM*
E(RM062X) = -614.089252599

Zero-point correction= 0.216996 (Hartree/Particle)
Thermal correction to Energy= 0.230241
Thermal correction to Enthalpy= 0.231186
Thermal correction to Gibbs Free Energy= 0.177106
Sum of electronic and ZPE= -613.872256
Sum of electronic and thermal Energies= -613.859011
Sum of electronic and thermal Enthalpies= -613.858067
Sum of electronic and thermal Free Energies= -613.912147

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	144.479	48.851	113.821

C,0,-0.4917136187,0.8826443258,-0.692366511
C,0,0.7795610387,0.7170491785,-0.2544883892
C,0,1.2868905282,-0.6330984488,-0.0701740205
C,0,0.5056987924,-1.7767264799,-0.4173201476
C,0,-0.7645780829,-1.5979468565,-0.8530160877
C,0,-1.394520443,-0.2703562179,-0.8771266625
O,0,1.6738302952,1.6736844201,0.0250890901
C,0,1.2373230261,3.0236786247,-0.1212898594
O,0,2.4875431666,-0.6995439722,0.3938099662
C,0,3.1380761517,-1.9709979921,0.6195881301
C,0,-2.3954027261,-0.2855154546,0.3986409292
O,0,-1.9295712016,-0.3423452892,1.5000557658
C,0,-3.8508222525,-0.2232162177,0.0570682314
H,0,-2.0347762476,-0.1493314675,-1.756012745
H,0,0.93535157,-2.7672923004,-0.344361866
H,0,-1.371358847,-2.4576261962,-1.1233027254
H,0,-0.9075832264,1.8730404044,-0.8400318465
H,0,2.0877891237,3.6407916949,0.1583604236
H,0,0.9563769354,3.2236105464,-1.1599546478
H,0,0.3927844277,3.2247309658,0.5450649836
H,0,4.0982360266,-1.7167353911,1.0584587799
H,0,2.54430581,-2.5673373554,1.3127583886
H,0,3.2749777854,-2.4821610819,-0.3339243057

H,0,-4.1079696241,-1.0707956947,-0.5861765676
H,0,-4.4462525579,-0.242052518,0.9688349865
H,0,-4.0472851679,0.6906825285,-0.5120294486

*MP2/6-31+G**/PCM*
EUMP2 = -0.61255254184746D+03

Zero-point correction= 0.217796 (Hartree/Particle)
Thermal correction to Energy= 0.231424
Thermal correction to Enthalpy= 0.232369
Thermal correction to Gibbs Free Energy= 0.177471
Sum of electronic and ZPE= -612.334746
Sum of electronic and thermal Energies= -612.321118
Sum of electronic and thermal Enthalpies= -612.320173
Sum of electronic and thermal Free Energies= -612.375071

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 145.221 49.838 115.541

6 -0.566223 1.083464 -0.712944
6 0.698892 0.827270 -0.241285
6 1.149209 -0.542882 -0.169557
6 0.357200 -1.611805 -0.679059
6 -0.904696 -1.349146 -1.131371
6 -1.488426 -0.027243 -0.945682
8 1.627236 1.730755 0.128471
6 1.225520 3.115841 0.067231
8 2.336834 -0.699001 0.355617
6 2.916935 -2.035354 0.465204
6 -2.243927 -0.233301 0.530669
8 -1.570785 -0.431759 1.513296
6 -3.732276 -0.128846 0.446280
1 -2.282866 0.206989 -1.650961
1 0.759962 -2.612092 -0.724884
1 -1.524877 -2.150223 -1.514439
1 -0.951316 2.091413 -0.778117
1 2.088668 3.672181 0.412607
1 0.983476 3.392424 -0.958469
1 0.373582 3.289830 0.723482
1 3.863950 -1.870478 0.962203
1 2.266843 -2.663171 1.067885
1 3.067659 -2.445252 -0.529455
1 -4.101492 -0.865462 -0.268286
1 -4.165600 -0.295585 1.428558
1 -3.997507 0.861480 0.073882

Saddle Point for 1,2-Migration (Structure **13**‡)
*B3LYP/6-31+G**/PCM G03*
Done with Gaussian 03 defaults.
E(RB+HF-LYP) = -614.357621035

Zero-point correction= 0.211456 (Hartree/Particle)
Thermal correction to Energy= 0.225099
Thermal correction to Enthalpy= 0.226043
Thermal correction to Gibbs Free Energy= 0.170760
Sum of electronic and ZPE= -614.146165
Sum of electronic and thermal Energies= -614.132522
Sum of electronic and thermal Enthalpies= -614.131578
Sum of electronic and thermal Free Energies= -614.186861

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 141.252 49.352 116.354

6 -0.145166 -1.416156 -0.728393
6 0.948688 -0.721840 -0.224860
6 0.946841 0.725528 -0.223095
6 -0.148090 1.420120 -0.726803
6 -1.267675 0.711223 -1.190770
6 -1.268635 -0.707332 -1.187569
8 2.060345 -1.279872 0.267479
6 2.167927 -2.713930 0.295699
8 2.055439 1.285328 0.272089
6 2.158851 2.719796 0.306071
6 -2.335872 -0.016351 0.700970
8 -1.611519 -0.022174 1.607607
6 -3.787861 0.007624 0.423951
1 -2.085025 -1.252991 -1.658310
1 -0.163116 2.504120 -0.749553
1 -2.087931 1.255928 -1.655879
1 -0.159679 -2.500145 -0.753090
1 3.142387 -2.919754 0.736837
1 1.377363 -3.147333 0.916862
1 2.123191 -3.123419 -0.718611
1 3.131657 2.926335 0.750526
1 2.115455 3.133066 -0.706646
1 1.365681 3.148110 0.927352
1 -4.317826 -0.066175 1.379383
1 -4.035993 0.946770 -0.081910
1 -4.054327 -0.822853 -0.235567

*B3LYP/6-31+G**/PCM G09*
E(RB3LYP) = -614.357958927

Zero-point correction= 0.212468 (Hartree/Particle)
Thermal correction to Energy= 0.226002
Thermal correction to Enthalpy= 0.226946
Thermal correction to Gibbs Free Energy= 0.172427
Sum of electronic and ZPE= -614.145491
Sum of electronic and thermal Energies= -614.131957

Sum of electronic and thermal Enthalpies= -614.131013
Sum of electronic and thermal Free Energies= -614.185532

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 141.818 49.303 114.746

C,0,-0.1417530477,-1.4109306287,-0.7485252926
C,0,0.9506479865,-0.7192585844,-0.2362555881
C,0,0.9504389556,0.7263848635,-0.2306657058
C,0,-0.1421516618,1.4216866832,-0.7376025032
C,0,-1.2609487349,0.7153470268,-1.2070160198
C,0,-1.2607622408,-0.7013025833,-1.2124594152
O,0,2.0573306933,-1.2827922897,0.2618124778
C,0,2.1566275033,-2.7177540477,0.2962233954
O,0,2.056946493,1.2863704799,0.2717668422
C,0,2.1558054331,2.7210528262,0.3173276819
C,0,-2.343815948,-0.0006619369,0.7240916856
O,0,-1.596789867,-0.0039542069,1.6083560059
C,0,-3.7904667441,0.000251634,0.4387610116
H,0,-2.0804369382,-1.2414141529,-1.6741393534
H,0,-0.1496429393,2.5035816726,-0.753167971
H,0,-2.0807825674,1.2587721558,-1.6645061171
H,0,-0.1489430679,-2.492675259,-0.7724366948
H,0,3.1258891896,-2.9272789497,0.7451507338
H,0,1.3596401504,-3.1428858942,0.913381691
H,0,2.1174629914,-3.1312330803,-0.7157612159
H,0,3.1249899186,2.9273786453,0.7678998535
H,0,2.1165446036,3.1423672082,-0.6914156227
H,0,1.3586688576,3.1411328904,0.9377432012
H,0,-4.3208570174,-0.0034582538,1.3953085235
H,0,-4.0443707132,0.8901957836,-0.1416653085
H,0,-4.0441612882,-0.8852990021,-0.1484362954

*M062X/6-31+G**/PCM*
E(RM062X) = -614.079939849

Zero-point correction= 0.215457 (Hartree/Particle)
Thermal correction to Energy= 0.228482
Thermal correction to Enthalpy= 0.229426
Thermal correction to Gibbs Free Energy= 0.176564
Sum of electronic and ZPE= -613.864483
Sum of electronic and thermal Energies= -613.851458
Sum of electronic and thermal Enthalpies= -613.850514
Sum of electronic and thermal Free Energies= -613.903376

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 143.375 48.397 111.258

6 -0.165912 -1.415227 -0.746766
6 0.918949 -0.720439 -0.238396
6 0.919258 0.720259 -0.238285
6 -0.165308 1.415628 -0.746559
6 -1.285601 0.705264 -1.204101
6 -1.285952 -0.704271 -1.204116
8 2.022470 -1.275136 0.262661
6 2.099916 -2.699513 0.302523
8 2.023010 1.274404 0.262840
6 2.101146 2.698746 0.302768
6 -2.246622 0.000062 0.743469
8 -1.455623 0.000173 1.574078
6 -3.698544 0.000187 0.495781
1 -2.115504 -1.243882 -1.649821
1 -0.172526 2.497612 -0.767158
1 -2.114973 1.245312 -1.649633
1 -0.173620 -2.497205 -0.767552
1 3.064594 -2.927258 0.750114
1 1.295301 -3.108043 0.920932
1 2.050088 -3.115246 -0.707817
1 3.065999 2.925997 0.750229
1 2.051364 3.114540 -0.707548
1 1.296821 3.107630 0.921316
1 -4.194038 -0.000235 1.469102
1 -3.960060 0.890797 -0.077866
1 -3.960272 -0.889726 -0.078835

*MP2/6-31+G**/PCM*
EUMP2 = -0.61255126983440D+03

Zero-point correction= 0.215875 (Hartree/Particle)
Thermal correction to Energy= 0.229421
Thermal correction to Enthalpy= 0.230366
Thermal correction to Gibbs Free Energy= 0.176181
Sum of electronic and ZPE= -612.335395
Sum of electronic and thermal Energies= -612.321848
Sum of electronic and thermal Enthalpies= -612.320904
Sum of electronic and thermal Free Energies= -612.375089

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 143.964 49.604 114.042

C,0,-0.1488823684,-1.4115542915,-0.8057602855
C,0,0.9147516501,-0.7137273592,-0.2285508565
C,0,0.9143222699,0.7208060082,-0.2234710587
C,0,-0.149564271,1.422224843,-0.7958897508
C,0,-1.2578304005,0.7145806388,-1.2777671985
C,0,-1.2574769961,-0.701078783,-1.2827112073
O,0,2.0085756517,-1.2771979079,0.3183866243

C,0,2.0716868658,-2.7188044013,0.3251582093
O,0,2.0078099393,1.2809674773,0.3275680343
C,0,2.0702078858,2.7225172532,0.3444169004
C,0,-2.206671119,-0.0003707552,0.7352164302
O,0,-1.3749478734,-0.0028788953,1.549899024
C,0,-3.6572613388,-0.0000568358,0.4980164315
H,0,-2.074599126,-1.2367503408,-1.7504896498
H,0,-0.1547486543,2.5019036552,-0.8180608886
H,0,-2.0752056839,1.2531093571,-1.7418046114
H,0,-0.153557133,-2.491048603,-0.8356104246
H,0,3.0127064032,-2.9533860044,0.8088810668
H,0,1.2408752307,-3.1318135973,0.8959795929
H,0,2.0658249231,-3.1031297206,-0.6938306108
H,0,3.0111577858,2.9541890737,0.8296744588
H,0,2.0640277795,3.1139384504,-0.6718620289
H,0,1.2392447441,3.1311106629,0.9181923225
H,0,-4.1512265747,-0.0035235916,1.4687966094
H,0,-3.9173553684,0.8893840995,-0.0722969983
H,0,-3.9167542216,-0.8857874321,-0.0783101348

Variational TS **14**‡
B3LYP/6-31+G**/PCM
Done with Gaussian 03 Defaults
E(RB+HF-LYP) = -614.351933391

Zero-point correction= 0.210195 (Hartree/Particle)
Thermal correction to Energy= 0.224354
Thermal correction to Enthalpy= 0.225298
Thermal correction to Gibbs Free Energy= 0.167679
Sum of electronic and ZPE= -614.141738
Sum of electronic and thermal Energies= -614.127580
Sum of electronic and thermal Enthalpies= -614.126636
Sum of electronic and thermal Free Energies= -614.184254

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 140.784 49.984 121.268

C,0,-0.0497046261,-1.4156698719,0.9001168797
C,0,0.9715132715,-0.7154053404,0.2560565239
C,0,0.9554027172,0.7122421528,0.2543297825
C,0,-0.0812879296,1.3901141976,0.8968379098
C,0,-1.108407819,0.6747299324,1.5351663927
C,0,-1.0932794711,-0.7234088325,1.5356129313
O,0,2.020920167,-1.2889818072,-0.3849104638
C,0,2.1128831463,-2.7174770926,-0.3956276136
O,0,1.9913893273,1.3079164446,-0.3883977342
C,0,2.0519436195,2.7379124527,-0.4014762621
C,0,-2.537745438,-0.0407425446,-1.1209731149
O,0,-1.586027324,-0.1136107387,-1.7247561537

C,0,-3.8544887146,0.0493256299,-0.5555013606
H,0,-1.8634846069,-1.2851431621,2.0617536213
H,0,-0.1010630678,2.4743745017,0.9182635044
H,0,-1.8896424675,1.2200839108,2.0623966181
H,0,-0.0452763048,-2.500096652,0.9218758671
H,0,3.0231259029,-2.9472126837,-0.9498057864
H,0,2.1911748631,-3.1139841384,0.6229996285
H,0,1.250358578,-3.1642092061,-0.9035374919
H,0,2.9554067674,2.9867826472,-0.9584809502
H,0,1.1784711864,3.1650921385,-0.907526711
H,0,2.1243992501,3.1377007448,0.6163596164
H,0,-3.9256011896,0.9760459765,0.0277979415
H,0,-4.5712187878,0.0562005338,-1.3914706235
H,0,-4.0198270497,-0.820685193,0.0927580485

Acetyl Chloride / AlCl3 complex (Structure **16**)
*B3LYP/6-31+G**, Al cis to methyl group*
E(RB3LYP) = -2236.73973409

Zero-point correction= 0.053404 (Hartree/Particle)
Thermal correction to Energy= 0.064850
Thermal correction to Enthalpy= 0.065794
Thermal correction to Gibbs Free Energy= 0.011966
Sum of electronic and ZPE= -2236.686330
Sum of electronic and thermal Energies= -2236.674884
Sum of electronic and thermal Enthalpies= -2236.673940
Sum of electronic and thermal Free Energies= -2236.727768

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 40.694 34.849 113.291

C,0,0.7991542254,1.8195368624,-0.6805643119
Cl,0,1.7556125754,2.6263961942,0.5191050591
O,0,0.9401591719,0.6027548321,-0.7835457592
C,0,-0.1004936174,2.6693572052,-1.5009581228
H,0,-0.705769016,3.3040611026,-0.8478964304
H,0,0.5214170875,3.3351270558,-2.1113923155
H,0,-0.7308000673,2.0527476107,-2.1405928695
Al,0,0.4970297191,-1.0199532783,-1.6508342963
Cl,0,-1.38696204,-0.7023533811,-2.6138532049
Cl,0,2.1369809761,-1.2790825568,-2.991798599
Cl,0,0.4184729853,-2.4037446467,-0.0301411497

*B3LYP/6-31+G**, Al trans to methyl group*
E(RB3LYP) = -2236.74051235

Zero-point correction= 0.053363 (Hartree/Particle)
Thermal correction to Energy= 0.063877
Thermal correction to Enthalpy= 0.064821

Thermal correction to Gibbs Free Energy= 0.014441
Sum of electronic and ZPE= -2236.687149
Sum of electronic and thermal Energies= -2236.676635
Sum of electronic and thermal Enthalpies= -2236.675691
Sum of electronic and thermal Free Energies= -2236.726072

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 40.084 32.859 106.035

C,0,1.3910330982,1.8026538068,-0.608499861
Cl,0,2.0773601179,2.4701119655,0.8360934679
O,0,1.2657983163,0.5837814017,-0.7259449997
C,0,0.9754276774,2.7590447041,-1.6642966864
H,0,0.2354713497,3.4522843199,-1.2507681771
H,0,1.8406165991,3.3571493996,-1.968935166
H,0,0.5632190953,2.2151928333,-2.5134123106
Al,0,1.5451347179,-1.0968934069,0.1220108152
Cl,0,3.6557375444,-1.196127931,0.4331230694
Cl,0,0.3713443443,-1.0002109399,1.9036629
Cl,0,0.8082951395,-2.4643521532,-1.3413310517

*M062X/6-31+G**, Al cis to methyl group*
E(RM062X) = -2236.50927812

Zero-point correction= 0.054296 (Hartree/Particle)
Thermal correction to Energy= 0.065515
Thermal correction to Enthalpy= 0.066459
Thermal correction to Gibbs Free Energy= 0.013911
Sum of electronic and ZPE= -2236.454982
Sum of electronic and thermal Energies= -2236.443763
Sum of electronic and thermal Enthalpies= -2236.442819
Sum of electronic and thermal Free Energies= -2236.495367

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 41.111 34.413 110.597

C,0,0.6780851148,1.76988254,-0.5162307699
Cl,0,1.1871362693,2.6661137428,0.8492396156
O,0,0.7629372173,0.5468493317,-0.4429313937
C,0,0.1739684351,2.5391920613,-1.6796889723
H,0,-0.6790508566,3.1421909585,-1.3544604636
H,0,0.9579717206,3.227248038,-2.0091795917
H,0,-0.1164502817,1.8734926951,-2.4916323918
Al,0,0.3740339276,-0.9144232273,-1.5701604788
Cl,0,-1.703995505,-0.7031724428,-1.9468425316
Cl,0,1.5911424851,-0.5579596851,-3.2720241294
Cl,0,0.9190234735,-2.5845670121,-0.3985608928

*M062X/6-31+G**, Al trans to methyl group*
E(RM062X) = -2236.51015387

Zero-point correction= 0.053896 (Hartree/Particle)
Thermal correction to Energy= 0.064339
Thermal correction to Enthalpy= 0.065283
Thermal correction to Gibbs Free Energy= 0.015168
Sum of electronic and ZPE= -2236.456258
Sum of electronic and thermal Energies= -2236.445815
Sum of electronic and thermal Enthalpies= -2236.444871
Sum of electronic and thermal Free Energies= -2236.494986

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	40.373	32.605	105.476

C,0,1.3803926711,1.741534703,-0.6481746284
Cl,0,2.0917930385,2.2965425971,0.8108638929
O,0,1.2076492621,0.5394114203,-0.8295108889
C,0,0.9974553723,2.763406393,-1.6483823635
H,0,0.2895485305,3.4584754727,-1.1878496157
H,0,1.8876746792,3.3361895529,-1.9238912583
H,0,0.5600355951,2.2768537368,-2.517858317
Al,0,1.5206608591,-1.0671651535,0.1138334678
Cl,0,3.6217821602,-1.0883130938,0.3974907559
Cl,0,0.3791709762,-0.8453620638,1.8868461336
Cl,0,0.7932748557,-2.5289395648,-1.2316651784

Acylation Transition Structure **17**‡
*B3LYP/6-31+G**, Conformation A*
E(RB3LYP) = -2583.51744739

Zero-point correction= 0.188120 (Hartree/Particle)
Thermal correction to Energy= 0.206970
Thermal correction to Enthalpy= 0.207914
Thermal correction to Gibbs Free Energy= 0.137525
Sum of electronic and ZPE= -2583.329328
Sum of electronic and thermal Energies= -2583.310478
Sum of electronic and thermal Enthalpies= -2583.309533
Sum of electronic and thermal Free Energies= -2583.379923

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	129.875	64.882	148.147

C,0,-1.3031299474,2.2785946648,-0.3472644046
C,0,-1.6531307172,1.6858541672,-1.6042825661
C,0,0.7014973423,1.8565708453,-0.2384331107
Cl,0,1.1295382192,2.7466733681,1.31104774
O,0,0.812804121,0.5900054085,-0.1342949106

C,0,1.2802927987,2.5863419287,-1.431477626
C,0,-2.2338855822,0.4415180515,-1.6767367068
C,0,-1.8155963652,1.6492645884,0.8399022723
H,0,-1.4078009972,2.2072549144,-2.5237488726
H,0,-1.1573383563,3.3543908379,-0.3228949135
H,0,0.9490222015,3.6237566407,-1.4717437865
H,0,2.3707441828,2.5730830366,-1.3250623006
H,0,1.0120705724,2.0664284649,-2.3523689728
C,0,-2.5920573982,-0.2196462866,-0.4728437437
H,0,-2.4303841377,-0.0142145708,-2.638355587
O,0,-3.1364064155,-1.4287761157,-0.4227068357
C,0,-2.4053618694,0.416371675,0.7859827181
H,0,-1.6698881376,2.1345073378,1.7984749788
H,0,-2.743421855,-0.0989735581,1.6779689423
C,0,-3.3742183889,-2.1807142778,-1.6338406221
H,0,-3.7753245881,-3.1349687232,-1.2986905516
H,0,-4.1055004314,-1.6661770693,-2.2620115794
H,0,-2.4380104553,-2.3359336932,-2.1742903387
Al,0,1.6453741775,-0.898499436,-0.7382860573
Cl,0,3.7367591236,-0.6838247566,-0.2662973978
Cl,0,0.7322035174,-2.5368727768,0.3122808609
Cl,0,1.3343163865,-1.0453266657,-2.8703446285

*B3LYP/6-31+G**, Conformation B*
E(RB3LYP) = -2583.51737802

Zero-point correction= 0.187961 (Hartree/Particle)
Thermal correction to Energy= 0.206856
Thermal correction to Enthalpy= 0.207800
Thermal correction to Gibbs Free Energy= 0.136596
Sum of electronic and ZPE= -2583.329417
Sum of electronic and thermal Energies= -2583.310522
Sum of electronic and thermal Enthalpies= -2583.309578
Sum of electronic and thermal Free Energies= -2583.380782

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 129.804 64.875 149.863

C,0,-0.9310002835,2.0887400967,-0.4018243165
C,0,-1.3616772265,1.5169204331,-1.6437145679
C,0,1.055243732,1.7216534521,-0.195241635
Cl,0,1.1789738823,-0.0882396676,-0.1560594063
O,0,1.3582906113,2.2547225051,0.9352722893
C,0,1.6518414398,2.2894875704,-1.4661735362
C,0,-2.1310145773,0.3774782922,-1.689487863
C,0,-1.4964706653,1.5408634239,0.8026272175
H,0,-1.0522138183,1.9797308821,-2.575145212
H,0,-0.7172081876,3.1553759304,-0.4031137287
H,0,2.7402978197,2.1995418675,-1.3803085293

H,0,1.3221659426,1.7460486348,-2.3496548122
H,0,1.3963363338,3.3478250505,-1.5595747213
C,0,-2.5838850569,-0.1943216622,-0.4725905107
H,0,-2.404306023,-0.0575520947,-2.642139348
O,0,-3.3206352015,-1.2973262901,-0.3987338231
C,0,-2.2747289469,0.4159728745,0.7741767621
H,0,-1.2506334375,2.0003799862,1.7540712574
H,0,-2.668847841,-0.0323371048,1.6793891088
C,0,-3.7049518095,-2.0049792107,-1.5980551866
H,0,-4.2747032702,-2.8638023008,-1.2492808624
H,0,-4.3321499673,-1.3700969708,-2.2285662237
H,0,-2.8187458148,-2.338302814,-2.1433740056
Al,0,1.961195178,3.7964270925,1.6651843515
Cl,0,0.8082712512,5.3992417389,0.7819464487
Cl,0,1.5940363551,3.6074467214,3.7742657696
Cl,0,4.0578845815,3.9757395635,1.2083430837

*M062X/6-31+G**, Conformation A*
E(RM062X) = -2583.14280974

Zero-point correction= 0.190751 (Hartree/Particle)
Thermal correction to Energy= 0.208957
Thermal correction to Enthalpy= 0.209901
Thermal correction to Gibbs Free Energy= 0.143101
Sum of electronic and ZPE= -2582.952059
Sum of electronic and thermal Energies= -2582.933853
Sum of electronic and thermal Enthalpies= -2582.932909
Sum of electronic and thermal Free Energies= -2582.999708

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 131.123 63.884 140.592

C,0,-1.3495643748,2.3979223048,-0.3530408417
C,0,-1.6350715386,1.7692268284,-1.5993745327
C,0,0.5984859592,1.8037244201,-0.1847350526
Cl,0,1.0523268238,2.6533084184,1.3317050571
O,0,0.5672455696,0.5360721533,-0.0619191348
C,0,1.2629830444,2.4380986989,-1.3807701108
C,0,-2.1277644152,0.4889350024,-1.6528983228
C,0,-1.8784980467,1.7918147236,0.8322768782
H,0,-1.3889937468,2.2823546385,-2.5242034723
H,0,-1.1604449371,3.4674227893,-0.3443840145
H,0,1.0336816184,3.5008878555,-1.4529173049
H,0,2.3437691106,2.3169942316,-1.2435829558
H,0,0.9594214796,1.9173463534,-2.2902822726
C,0,-2.4636391877,-0.1623871683,-0.4406489954
H,0,-2.259844047,-0.0064487626,-2.6057888976
O,0,-2.904096344,-1.4044833432,-0.3764866528
C,0,-2.3837965405,0.5248387351,0.8002531726

H,0,-1.7948658183,2.3177159498,1.777366981
H,0,-2.7212127333,0.0116640326,1.6935378444
C,0,-2.946528435,-2.2003815949,-1.5676393912
H,0,-3.2315304725,-3.1967157091,-1.2388092124
H,0,-3.6939150078,-1.8038375714,-2.2592646354
H,0,-1.9586999016,-2.2292146523,-2.0358603395
Al,0,1.2199929016,-0.9306788323,-0.8758034638
Cl,0,3.3307114048,-0.8821630296,-0.5459162147
Cl,0,0.2217622065,-2.5463512822,0.0927739895
Cl,0,0.7712524285,-0.88897719,-2.9739061046

*M062X/6-31+G**, Conformation B*
E(RM062X) = -2583.13785239

Zero-point correction= 0.190666 (Hartree/Particle)
Thermal correction to Energy= 0.208835
Thermal correction to Enthalpy= 0.209779
Thermal correction to Gibbs Free Energy= 0.142444
Sum of electronic and ZPE= -2582.947186
Sum of electronic and thermal Energies= -2582.929017
Sum of electronic and thermal Enthalpies= -2582.928073
Sum of electronic and thermal Free Energies= -2582.995408

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 131.046 63.820 141.718

C,0,-0.9723049875,2.1732836584,-0.407481527
C,0,-1.3804238865,1.5944951981,-1.6442604054
C,0,0.9672838517,1.6439562473,-0.1636028007
Cl,0,0.9463288512,-0.1316505453,-0.1783340754
O,0,1.2706843064,2.1254854261,0.9881727186
C,0,1.6146281334,2.2237833543,-1.3971857472
C,0,-2.1168709929,0.4356184911,-1.6867860179
C,0,-1.5392993595,1.6405936802,0.7943291307
H,0,-1.0709435836,2.0596072176,-2.5755259848
H,0,-0.6927375775,3.2245510493,-0.4090231202
H,0,2.692812089,2.0625135003,-1.2911201885
H,0,1.2647823334,1.7337935134,-2.3035644422
H,0,1.4249999888,3.2994365102,-1.4483358775
C,0,-2.5527343138,-0.1365619977,-0.4679445876
H,0,-2.3701674616,-0.0180478174,-2.6361700348
O,0,-3.2365853839,-1.2656541223,-0.3917770315
C,0,-2.2859782386,0.497693958,0.7730083402
H,0,-1.3043001905,2.1183008046,1.7410888422
H,0,-2.6765869265,0.0439374145,1.6766760664
C,0,-3.5522534423,-1.9864245807,-1.5884934315
H,0,-4.078874236,-2.8780432743,-1.2575614588
H,0,-4.1997400913,-1.3868074714,-2.2325278693
H,0,-2.6368804214,-2.2654479829,-2.1158162344

Al,0,1.9208475947,3.6876094854,1.6056846859
Cl,0,0.63492767,5.2226731331,0.8286605792
Cl,0,1.8116113292,3.5371588756,3.7272441763
Cl,0,3.9191399457,3.9107842743,0.8828842951

Acylation Transition Structure **18**‡
*B3LYP/6-31+G**, Conformation A*
E(RB3LYP) = -2698.04447383

Zero-point correction= 0.220628 (Hartree/Particle)
Thermal correction to Energy= 0.242112
Thermal correction to Enthalpy= 0.243056
Thermal correction to Gibbs Free Energy= 0.166830
Sum of electronic and ZPE= -2697.823846
Sum of electronic and thermal Energies= -2697.802362
Sum of electronic and thermal Enthalpies= -2697.801417
Sum of electronic and thermal Free Energies= -2697.877644

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	151.928	74.047	160.432

C,0,-1.3171030195,1.4907031165,-1.3984740443
C,0,-0.9664085527,0.3981862074,-2.2475939553
C,0,0.5121865114,1.8929062343,-0.543513007
Cl,0,0.0696297925,3.4037711692,0.4067301468
O,0,0.7945769284,0.8992698806,0.2048451307
C,0,1.4002178487,2.2561350773,-1.712870165
C,0,-1.2200148385,-0.9013814472,-1.8684681928
C,0,-2.1606269233,1.222850025,-0.2658465273
H,0,-0.4450288339,0.5872537557,-3.1795822944
H,0,-1.4009842372,2.4733195656,-1.8530176741
H,0,0.9254052579,2.9809239568,-2.3742094476
H,0,2.3140856535,2.7040641454,-1.3066054813
H,0,1.6670038509,1.3540735937,-2.2655304897
C,0,-1.9329089581,-1.1571128384,-0.6758649881
H,0,-0.8854246202,-1.7246713658,-2.486073586
O,0,-2.2155528577,-2.3668472554,-0.2199611457
C,0,-2.4333096214,-0.0659409201,0.1223817948
H,0,-2.5187710651,2.0591519908,0.3196418593
O,0,-3.1592547377,-0.4394396637,1.1997442508
C,0,-1.7689164327,-3.5400084759,-0.9349818277
H,0,-2.1231032868,-4.3813433686,-0.3429224447
H,0,-2.2142473461,-3.5684312154,-1.9325015609
H,0,-0.6783706398,-3.5552174605,-0.994772639
C,0,-3.6721662269,0.5895538806,2.0562283748
H,0,-4.1969873308,0.0679225407,2.8554163089
H,0,-2.8571439277,1.1876591322,2.4764794298
H,0,-4.3718049744,1.2350338561,1.514363917
Al,0,2.0618258973,-0.2894051776,0.7083392667

Cl,0,3.5957774097,0.8238399435,1.7343746344
Cl,0,1.0576057098,-1.683221338,2.0007710199
Cl,0,2.8531455704,-1.2637945449,-1.0499316632

*B3LYP/6-31+G**, Conformation B*
E(RB3LYP) = -2698.04463980

Zero-point correction= 0.220657 (Hartree/Particle)
Thermal correction to Energy= 0.242077
Thermal correction to Enthalpy= 0.243021
Thermal correction to Gibbs Free Energy= 0.166870
Sum of electronic and ZPE= -2697.823983
Sum of electronic and thermal Energies= -2697.802563
Sum of electronic and thermal Enthalpies= -2697.801619
Sum of electronic and thermal Free Energies= -2697.877770

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 151.905 73.958 160.274

C,0,-0.9432615944,2.0918046103,-0.3691127819
C,0,-1.3603903311,1.537835219,-1.6175337955
C,0,1.0481918048,1.7131930031,-0.1933770411
Cl,0,1.1559987174,-0.0961279246,-0.1285717831
O,0,1.3624934596,2.2570482685,0.930498541
C,0,1.6443342612,2.2605449521,-1.4731245852
C,0,-2.1291499438,0.3959665091,-1.6676747845
C,0,-1.5084588463,1.543966067,0.8351396564
H,0,-1.0441799951,2.0059317122,-2.5433363802
H,0,-0.7244499426,3.1574830022,-0.3570159285
H,0,2.7334214531,2.1809111313,-1.384227839
H,0,1.3194864872,1.6970969135,-2.3459347863
H,0,1.3827630537,3.3153081223,-1.5890348815
C,0,-2.5899763214,-0.1915997132,-0.4690758653
H,0,-2.3932167275,-0.0411939414,-2.6218349897
O,0,-3.3181279034,-1.2970839998,-0.4112563254
C,0,-2.2877457813,0.4133357523,0.8035088358
H,0,-1.2524899059,2.0077593423,1.7792403078
O,0,-2.82537602,-0.2171425909,1.8723182912
C,0,-3.6825697811,-1.9953586174,-1.6217921184
H,0,-4.254799381,-2.8582393066,-1.2872417432
H,0,-4.3024175223,-1.3572291568,-2.2563021117
H,0,-2.7874096755,-2.3223086968,-2.1564709859
C,0,-2.5596079208,0.3204953073,3.1751998783
H,0,-3.0775670573,-0.3371030715,3.8719778441
H,0,-1.4856387558,0.3142263713,3.3874895363
H,0,-2.9538019213,1.3383804101,3.2640662572
Al,0,1.9675036528,3.8070269163,1.6379486108
Cl,0,0.8051470115,5.4025061419,0.7528675206
Cl,0,1.6170606328,3.6388700035,3.752868923

Cl,0,4.060705794,3.9893572633,1.1660245239

*M062X/6-31+G**, Conformation A*
E(RM062X) = -2697.62425753

Zero-point correction= 0.223892 (Hartree/Particle)
Thermal correction to Energy= 0.244542
Thermal correction to Enthalpy= 0.245486
Thermal correction to Gibbs Free Energy= 0.173277
Sum of electronic and ZPE= -2697.400365
Sum of electronic and thermal Energies= -2697.379716
Sum of electronic and thermal Enthalpies= -2697.378771
Sum of electronic and thermal Free Energies= -2697.450981

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	153.452	72.747	151.978

C,0,-1.3562424254,2.3932897517,-0.3454175165
C,0,-1.6244280058,1.7685545745,-1.5920972404
C,0,0.5930060231,1.8084043694,-0.2006415339
Cl,0,1.046177891,2.6594795715,1.3190560997
O,0,0.5598509222,0.540090243,-0.0689387458
C,0,1.2726977197,2.4388774082,-1.3899942891
C,0,-2.1206937892,0.4864596348,-1.6404816644
C,0,-1.8889297156,1.7987981488,0.8452432177
H,0,-1.3654112006,2.2767485163,-2.5155374425
H,0,-1.1741334269,3.4641568176,-0.3350745304
H,0,1.0358640408,3.4995555932,-1.4726305223
H,0,2.3521739784,2.3294357638,-1.2350140549
H,0,0.9897867753,1.9106837731,-2.3019172835
C,0,-2.4643550798,-0.1676769283,-0.4407664398
H,0,-2.2411866457,-0.0179534029,-2.5902080098
O,0,-2.9078588853,-1.4039428126,-0.3727316154
C,0,-2.3841999202,0.5240119293,0.8187447702
H,0,-1.7973060325,2.338937381,1.7792628555
O,0,-2.8242141965,-0.1825023313,1.8762123862
C,0,-2.9555696804,-2.1977604639,-1.5653811677
H,0,-3.2550461134,-3.1901786369,-1.2375224994
H,0,-3.6951662704,-1.7901013908,-2.2586616415
H,0,-1.9660586702,-2.237964503,-2.0291994387
C,0,-2.7088596133,0.4336594899,3.1534446545
H,0,-3.0785594803,-0.2965495937,3.8702424457
H,0,-1.6627365824,0.6735484363,3.3710644907
H,0,-3.3189102313,1.3417303965,3.2015508245
Al,0,1.218028336,-0.9238986156,-0.8782857043
Cl,0,3.3304272788,-0.8730541614,-0.5509347544
Cl,0,0.224863939,-2.5434145719,0.0893394928
Cl,0,0.774202061,-0.8818623868,-2.9779251429

*M062X/6-31+G**, Conformation B*
E(RM062X) = -2697.61943773

Zero-point correction= 0.223419 (Hartree/Particle)
Thermal correction to Energy= 0.244319
Thermal correction to Enthalpy= 0.245263
Thermal correction to Gibbs Free Energy= 0.170978
Sum of electronic and ZPE= -2697.396018
Sum of electronic and thermal Energies= -2697.375119
Sum of electronic and thermal Enthalpies= -2697.374175
Sum of electronic and thermal Free Energies= -2697.448459

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	153.312	72.917	156.345

C,0,-0.9928300249,2.1661922267,-0.391245134
C,0,-1.3957897376,1.6003186813,-1.6289472041
C,0,0.9515152758,1.639604561,-0.1886400307
Cl,0,0.9268580745,-0.1365452345,-0.2102734726
O,0,1.2592883843,2.1109312258,0.9671529483
C,0,1.5982004731,2.2267050626,-1.4191528279
C,0,-2.1293820107,0.4357411826,-1.6680681982
C,0,-1.5451820084,1.6331228133,0.8185376809
H,0,-1.0876665795,2.069539142,-2.5581419591
H,0,-0.718127392,3.2188754648,-0.3845616489
H,0,2.6790163105,2.0869445953,-1.3061227583
H,0,1.2645852244,1.7258531095,-2.3260224624
H,0,1.3876749099,3.2979546655,-1.4778893746
C,0,-2.5541763577,-0.1522859153,-0.4618095448
H,0,-2.3815191919,-0.0216131874,-2.6160050815
O,0,-3.2222120084,-1.2864113376,-0.3841751389
C,0,-2.2783344842,0.4776892529,0.8002953298
H,0,-1.2902917753,2.1142714401,1.7563449319
O,0,-2.7780989067,-0.1663134166,1.8717340496
C,0,-3.5368016652,-1.9996812629,-1.5853993206
H,0,-4.0493608175,-2.900842251,-1.2582944762
H,0,-4.1965109849,-1.4013742491,-2.2183077301
H,0,-2.6209773135,-2.2612685226,-2.1208485232
C,0,-2.4840231496,0.386312813,3.1502134366
H,0,-2.9447285203,-0.2813488202,3.8753698822
H,0,-1.4019007905,0.4246315437,3.3141205985
H,0,-2.9113921877,1.3897731641,3.245945552
Al,0,1.8762368663,3.6700441081,1.6174307387
Cl,0,0.6773535495,5.2253083272,0.7454764477
Cl,0,1.5878829977,3.5292667293,3.7252818696
Cl,0,3.9271648404,3.8542640885,1.0522314202

<u>Bromination Transition Structure (Structure **20**‡)</u>
B3LYP/6-31G*/PCM

Done with Gaussian 03
E(RB+HF-LYP) = -6521.08477327

Zero-point correction= 0.420094 (Hartree/Particle)
Thermal correction to Energy= 0.459026
Thermal correction to Enthalpy= 0.459970
Thermal correction to Gibbs Free Energy= 0.333369
Sum of electronic and ZPE= -6520.664679
Sum of electronic and thermal Energies= -6520.625747
Sum of electronic and thermal Enthalpies= -6520.624803
Sum of electronic and thermal Free Energies= -6520.751405

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 288.043 123.331 266.456

6 3.235636 0.265487 0.968131
6 4.361564 0.461853 0.213640
6 4.840461 -0.615028 -0.624019
6 4.159048 -1.851002 -0.675273
6 3.028870 -2.038425 0.084703
6 2.495748 -0.975591 0.902529
8 5.105826 1.584550 0.162668
6 4.647293 2.713815 0.920008
8 5.929819 -0.334906 -1.315640
6 6.500349 -1.317305 -2.202899
35 0.723820 -0.492966 -0.294750
1 1.931557 -1.255410 1.790237
1 4.522418 -2.651581 -1.309713
1 2.508262 -2.992604 0.065080
1 2.839633 1.052978 1.596031
1 5.349908 3.516766 0.693810
1 3.632651 2.996961 0.620023
1 4.675075 2.494118 1.994583
1 7.368004 -0.828617 -2.644496
1 6.811592 -2.203175 -1.641375
1 5.782300 -1.588335 -2.982481
35 -1.758700 0.335146 -1.295297
1 -2.427976 -1.985363 -1.123822
8 -2.874642 -2.863717 -1.103712
6 -2.185865 -3.679208 -0.282804
8 -1.163704 -3.350457 0.287226
6 -2.843913 -5.034737 -0.175240
1 -2.925567 -5.492111 -1.167132
1 -2.259320 -5.678659 0.483006
1 -3.860532 -4.926340 0.218075
1 -0.989827 2.393377 -0.231029
8 -0.961713 3.255283 0.245821
6 0.317346 3.615707 0.444995
8 1.267211 2.956551 0.062929

6 0.411599 4.919511 1.200132
1 0.016772 4.787593 2.213950
1 1.450940 5.245508 1.252448
1 -0.197557 5.685644 0.710039
1 -1.744847 -0.399088 1.152274
8 -2.230604 -0.729885 1.938744
6 -1.368916 -0.987749 2.936960
8 -0.179022 -0.736219 2.895255
6 -2.069371 -1.629118 4.110584
1 -2.963749 -1.059925 4.382421
1 -2.394596 -2.637247 3.829642
1 -1.388561 -1.690606 4.960563
1 -3.957563 0.923466 -0.458769
8 -4.846682 1.148391 -0.099067
6 -5.601827 1.607458 -1.116050
8 -5.193282 1.704959 -2.257111
6 -6.992284 1.972063 -0.654837
1 -6.939116 2.728735 0.135329
1 -7.571866 2.353377 -1.496309
1 -7.487321 1.091442 -0.231034

Transition Structure for Addition of Acetylium Ion to Benzene (Structure **19**‡)
B3LYP/6-31+G**/PCM
E(RB+HF-LYP) = -385.293479401

Zero-point correction= 0.145695 (Hartree/Particle)
Thermal correction to Energy= 0.154236
Thermal correction to Enthalpy= 0.155180
Thermal correction to Gibbs Free Energy= 0.111432
Sum of electronic and ZPE= -385.147784
Sum of electronic and thermal Energies= -385.139243
Sum of electronic and thermal Enthalpies= -385.138299
Sum of electronic and thermal Free Energies= -385.182048

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 96.785 31.082 92.076

C,0,0.5078116454,-0.8628731781,1.6090955574
C,0,1.5173269,-1.7934903681,1.3122095301
C,0,1.4366664796,-2.5465646519,0.1483386104
C,0,0.3076625974,-2.4003731287,-0.7027791842
C,0,-0.6603217129,-1.3939781848,-0.4364594662
C,0,-0.5670000816,-0.6474962804,0.7308027863
H,0,2.3592801792,-1.9169047187,1.9905249113
H,0,0.5712044393,-0.2813166388,2.5281458822
C,0,-0.8585570713,-3.9409446442,0.4259220823
O,0,-1.0246250709,-3.6881858311,1.536024497
C,0,-1.1222334386,-4.9390675382,-0.6212839037
H,0,-1.4787470399,-1.2339806034,-1.1375095291

H,0,0.3123924837,-2.8860905925,-1.6772527286
H,0,-1.6841188352,-4.4683229207,-1.4345775231
H,0,-0.1698338481,-5.3084094987,-1.0153324997
H,0,-1.6991398236,-5.7499273859,-0.1616063401
H,0,-1.3178140663,0.1046901207,0.964715936
H,0,2.2156392638,-3.2639759565,-0.1073466183

Model 22 (**15**)
ONIOM(B3LYP/6-31G*:AM1)
E(RB+HF-LYP) = -614.244235669

Zero-point correction= 0.848689 (Hartree/Particle)
Thermal correction to Energy= 0.993494
Thermal correction to Enthalpy= 0.994438
Thermal correction to Gibbs Free Energy= 0.509411
Sum of electronic and ZPE= -614.382591
Sum of electronic and thermal Energies= -614.237786
Sum of electronic and thermal Enthalpies= -614.236842
Sum of electronic and thermal Free Energies= -614.721869

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 623.427 403.283 1020.825

C,0,3.0128677978,-0.2450059019,-0.8738126553
C,0,2.0639169802,-1.0608528511,-1.5137092686
C,0,0.377831465,1.3555070838,-0.5501226636
O,0,0.5120506893,1.9336901671,-1.5214965686
C,0,-0.0619668257,0.8948008504,0.7450246649
C,0,1.7239408483,-0.8273289792,-2.8516266439
C,0,3.6260317406,0.8021132258,-1.5731234546
H,0,1.6237082512,-1.9049176511,-0.9867791668
H,0,3.3065149751,-0.4498120209,0.1530315974
H,0,-0.3723961295,-0.1555365184,0.6645010235
H,0,0.7790801489,0.9712655182,1.4482017309
H,0,-0.9040866185,1.5222394332,1.0825453349
C,0,2.3124352224,0.2266655252,-3.55312893
H,0,1.0008480556,-1.4704343436,-3.3408222314
O,0,2.0581999404,0.5470277444,-4.8348904014
C,0,3.2850575018,1.053923452,-2.9027818232
H,0,4.3701043188,1.4138289521,-1.0754464875
O,0,3.8081505014,2.0279329624,-3.6711486724
C,0,1.0757831376,-0.2061621678,-5.5466337093
H,0,1.031216163,0.2369447393,-6.5401442181
H,0,1.3661751216,-1.2601713878,-5.625514081
H,0,0.0927701738,-0.1289455447,-5.0644688348
C,0,4.7890106605,2.8951252531,-3.1030766129
H,0,5.0609298838,3.5890303922,-3.8969070292
H,0,4.3781387043,3.4532979104,-2.2530917041

H,0,5.6750605216,2.333888763,-2.7836439683
C,0,-0.796506191,6.6769567721,-4.3314508139
H,0,-0.3331770236,7.4906761871,-4.9337226847
H,0,-1.5797063479,6.1253419018,-4.9002399337
Cl,0,0.4571468873,5.542623281,-3.9038543587
Cl,0,-1.548728409,7.3985033595,-2.9347793765
C,0,-3.4033845438,2.6908069775,3.0402326263
Cl,0,-1.9897108949,1.9490801675,3.744386862
H,0,-3.4237449468,3.7607828395,3.346983372
Cl,0,-3.3782158234,2.6293405087,1.2948948321
H,0,-4.3016115716,2.1313649845,3.3928670095
Cl,0,3.9410007423,0.5596404903,5.6456089691
C,0,4.6939947342,1.5077895912,6.8994759488
H,0,5.7661807314,1.2139459357,6.958992572
Cl,0,4.6215398974,3.2196807472,6.5752058179
H,0,4.1519190462,1.3150514357,7.852559177
Cl,0,3.6273342412,-5.4391108546,2.4770434286
C,0,5.2175814314,-4.7383263376,2.6550857696
H,0,5.8791318374,-5.5058244154,3.1156949818
H,0,5.5722220503,-4.4235279328,1.6456565118
Cl,0,5.2099774004,-3.336314978,3.6892188397
Cl,0,-5.756035369,-1.1029687679,-2.6919516178
C,0,-7.0829853645,-0.3906121835,-1.8090734053
H,0,-7.2756913127,-1.0183674602,-0.9080932843
Cl,0,-6.7325558244,1.2312427254,-1.2775460747
H,0,-7.9631288638,-0.3493575257,-2.4895049803
Cl,0,0.5537388975,-2.5862775574,1.8152403546
C,0,1.6067381066,-2.2037664531,3.1536948087
H,0,2.3833000502,-3.0009058973,3.2255665226
Cl,0,2.4231899237,-0.6748691886,2.9288825886
H,0,0.9828687439,-2.1283747451,4.074400994
Cl,0,-5.2699105233,-4.3751492201,-2.2739969407
C,0,-4.7124477358,-5.9885240632,-1.9163408335
H,0,-5.0190248834,-6.2337342696,-0.873842812
H,0,-5.1632698854,-6.6813277252,-2.6620897422
Cl,0,-2.9793859104,-6.1370778641,-2.0156874302
Cl,0,-2.1926312082,0.5144424242,-3.2070398451
C,0,-3.3202783552,1.8339527977,-3.0115164634
Cl,0,-2.7338107663,3.0344222855,-1.8860149109
H,0,-3.455258578,2.3266857617,-4.0026543291
H,0,-4.273725124,1.4165058328,-2.6107456479
Cl,0,5.7105780538,-3.974493061,-1.1314346444
C,0,7.2344997619,-3.1319723748,-1.0988603108
Cl,0,7.787231389,-2.8233758473,0.5298032754
H,0,7.9971788394,-3.7662193641,-1.605659817
H,0,7.1034903268,-2.149818479,-1.610047928
Cl,0,7.5971198201,-1.2754021445,-4.3749898646
C,0,9.1406203806,-1.9018420907,-4.8900639856
Cl,0,9.8727601458,-2.9455732884,-3.7015469284
H,0,8.9778925982,-2.4965563054,-5.8170769755

H,0,9.8240249698,-1.0392723405,-5.0580986209
Cl,0,-4.7517898927,-5.062508064,1.7832842052
C,0,-3.4011777954,-5.6436398874,2.7256031318
Cl,0,-1.9925440974,-4.6340979511,2.5632001765
H,0,-3.7072374213,-5.646183383,3.7959091519
H,0,-3.1415621598,-6.6629298113,2.3607019388
Cl,0,2.1109690342,8.3585296158,2.0223512308
C,0,0.7582408956,9.2837566752,2.6189822495
Cl,0,-0.7716789828,8.5249537049,2.2689922485
H,0,0.8580007325,9.3674427258,3.7246016178
H,0,0.7735682512,10.2783852377,2.1188180781
Cl,0,6.5336933101,1.8622464062,0.8238427083
C,0,7.8835829834,0.9820388859,0.1561076349
Cl,0,7.7028156402,0.6690808916,-1.5490504729
H,0,8.799674627,1.5979650376,0.2992393737
H,0,7.9477887564,0.0005411513,0.680065667
Cl,0,-8.5727321949,-1.5128366298,1.6559223562
C,0,-8.4062278292,-3.2414022458,1.4877282629
Cl,0,-7.3555965018,-3.68332662,0.1695539157
H,0,-7.9660666513,-3.6388376442,2.4297051289
H,0,-9.4156335514,-3.6646782335,1.2832355644
Cl,0,0.1467945941,-5.9737072918,-0.5156047155
C,0,1.8429148742,-6.137420781,-0.8804114281
H,0,2.3827502508,-6.3316925931,0.0744698425
H,0,1.9600060716,-6.9719608834,-1.6076869138
Cl,0,2.5203805963,-4.7006364639,-1.5959720844
Cl,0,-5.5325053167,3.1973989825,-5.7994757729
C,0,-4.4049153219,3.9725116441,-6.8765951348
H,0,-4.711315697,5.0364065978,-6.9929894702
Cl,0,-2.7704184947,3.9456653583,-6.2625815213
H,0,-4.41515733,3.4229353755,-7.8448786574
Cl,0,-1.8126101232,-2.3298170227,4.9299393151
C,0,-1.6812994832,-0.9570036306,5.9955664527
Cl,0,-0.1913701265,-0.0797040158,5.770152849
H,0,-2.5254139642,-0.2649938492,5.7716142533
H,0,-1.7076888628,-1.3277534536,7.0448529992
Cl,0,-6.8520878717,1.9639501232,4.5232100949
C,0,-6.8085746468,0.2308301793,4.6911465715
Cl,0,-5.2105027691,-0.4255441527,4.4441933273
H,0,-7.1298078798,-0.0244055434,5.726003127
H,0,-7.4813420754,-0.2091903553,3.9195329055
Cl,0,3.344460027,2.273009117,1.8374067905
C,0,2.7906713276,3.2455511434,3.1831449859
Cl,0,1.063972957,3.1400748693,3.3967905229
H,0,3.283616947,2.8624661377,4.1077847152
H,0,3.0524074603,4.3058205816,2.967776047
Cl,0,-1.3746248597,-2.3058902067,-0.7891178911
C,0,-3.0052644578,-2.1386460948,-0.1844936819
Cl,0,-3.2849016584,-0.5639824406,0.5158477679
H,0,-3.7071533061,-2.2682833481,-1.0410124829

H,0,-3.1585099075,-2.9060011674,0.6099670164
Cl,0,-2.208909347,-2.329667,-4.8782363478
C,0,-1.5013407165,-3.9236859979,-4.8785246481
H,0,-1.9227693687,-4.4881789686,-4.0150241937
H,0,-1.7398703424,-4.4053010614,-5.8533326999
Cl,0,0.2322667939,-3.8855551529,-4.704759181
Cl,0,-1.0006945527,4.6390283557,0.4096106595
C,0,0.3231388051,5.6750961388,-0.0705972406
H,0,0.4149551473,6.4916116102,0.6834026994
Cl,0,1.8396781832,4.8094343537,-0.1244144907
H,0,0.1061885124,6.0609831674,-1.0944314831

Benzene
*B3LYP/6-31+G**/PCM*
E(RB+HF-LYP) = -232.273438661

Zero-point correction= 0.099611 (Hartree/Particle)
Thermal correction to Energy= 0.104024
Thermal correction to Enthalpy= 0.104968
Thermal correction to Gibbs Free Energy= 0.072131
Sum of electronic and ZPE= -232.173827
Sum of electronic and thermal Energies= -232.169415
Sum of electronic and thermal Enthalpies= -232.168471
Sum of electronic and thermal Free Energies= -232.201308

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 65.276 17.273 69.112

C,0,0.,0.,0.
C,0,0.,0.,1.4
C,0,1.2124356667,0.,2.1
C,0,2.424871,0.,1.4
C,0,2.424871,0.,0.
C,0,1.2124356667,0.,-0.7
H,0,-0.943102,0.,1.9445
H,0,1.2124356667,0.,3.189
H,0,3.367973,0.,1.9445
H,0,3.367973,0.,-0.5445
H,0,1.2124356667,0.,-1.789
H,0,-0.943102,0.,-0.544

*M062X/6-31+G**/PCM*
E(RM062X) = -232.154711628

Zero-point correction= 0.101088 (Hartree/Particle)
Thermal correction to Energy= 0.105479
Thermal correction to Enthalpy= 0.106423
Thermal correction to Gibbs Free Energy= 0.073620
Sum of electronic and ZPE= -232.053624

Sum of electronic and thermal Energies= -232.049232
Sum of electronic and thermal Enthalpies= -232.048288
Sum of electronic and thermal Free Energies= -232.081092

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 66.189 17.083 69.041

C,0,0.00386146,0.,0.0023115044
C,0,0.0038933679,0.,1.3978125944
C,0,1.2124649263,0.,2.0953479675
C,0,2.4210129625,0.,1.3977641376
C,0,2.420981153,0.,0.0022691708
C,0,1.2124065075,0.,-0.6952659222
H,0,-0.9362629551,0.,1.9409945146
H,0,1.2124874963,0.,3.1811116446
H,0,3.3611906694,0.,1.9409083192
H,0,3.3611323094,0.,-0.5409209541
H,0,1.2123928786,0.,-1.7810303054
H,0,-0.9363345533,0.,-0.5408026714

Bromine
*B3LYP/6-31+G**/PCM*
Done with Gaussian 03 defaults.
E(RB+HF-LYP) = -5143.42890672

Zero-point correction= 0.000735 (Hartree/Particle)
Thermal correction to Energy= 0.003488
Thermal correction to Enthalpy= 0.004432
Thermal correction to Gibbs Free Energy= -0.023425
Sum of electronic and ZPE= -5143.428172
Sum of electronic and thermal Energies= -5143.425419
Sum of electronic and thermal Enthalpies= -5143.424475
Sum of electronic and thermal Free Energies= -5143.452332

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 2.189 6.598 58.631

Br,0,0.,0.,-0.018358314
Br,0,0.,0.,2.308358314

*M062X/6-31+G**/PCM*
M062X/6-31+G**
E(RM062X) = -5143.56199789

Zero-point correction= 0.000797 (Hartree/Particle)
Thermal correction to Energy= 0.003519
Thermal correction to Enthalpy= 0.004463
Thermal correction to Gibbs Free Energy= -0.023302

Sum of electronic and ZPE= -5143.561201
Sum of electronic and thermal Energies= -5143.558479
Sum of electronic and thermal Enthalpies= -5143.557535
Sum of electronic and thermal Free Energies= -5143.585300

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 2.208 6.543 58.436

Br,0,0.,0.,-0.0947809149
Br,0,0.,0.,2.1947809149

Calculated Structures for the Hydroamination of Alkynes

Phenylacetylene
*m062x/6-31+g***
E(RM062X) = -308.274274150

Zero-point correction= 0.110531 (Hartree/Particle)
Thermal correction to Energy= 0.116879
Thermal correction to Enthalpy= 0.117823
Thermal correction to Gibbs Free Energy= 0.080171
Sum of electronic and ZPE= -308.163743
Sum of electronic and thermal Energies= -308.157395
Sum of electronic and thermal Enthalpies= -308.156451
Sum of electronic and thermal Free Energies= -308.194103

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 73.343 24.840 79.246

C,0,-0.0216592259,-0.0023326662,-0.0044708032
C,0,-0.0114624748,-0.0005544544,1.3974610983
C,0,1.1973772964,0.0013421831,2.0858275188
C,0,2.4033949576,0.0014477166,1.3857715191
C,0,2.3981634154,-0.0003581728,-0.0086929415
C,0,1.1933240255,-0.0022443004,-0.7040386173
H,0,-0.9547553634,-0.0006768628,1.9337511788
H,0,1.1983572826,0.002720363,3.1712171643
H,0,3.3450287643,0.0029304561,1.925612062
H,0,3.3353049043,-0.0002985861,-0.5562710214
H,0,1.1794782809,-0.0036845771,-1.7890326429
C,0,-1.2677511882,-0.0042773376,-0.7190058271
C,0,-2.3158507181,-0.0057861285,-1.3200925206
H,0,-3.2413809566,-0.0072336328,-1.8508551672

*m06/6-31+g***
E(RM06) = -308.166516402

Zero-point correction= 0.109128 (Hartree/Particle)
Thermal correction to Energy= 0.115561
Thermal correction to Enthalpy= 0.116505
Thermal correction to Gibbs Free Energy= 0.078737
Sum of electronic and ZPE= -308.057389
Sum of electronic and thermal Energies= -308.050955
Sum of electronic and thermal Enthalpies= -308.050011
Sum of electronic and thermal Free Energies= -308.087780

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 72.516 25.312 79.491

C,0,-0.0238136129,-0.0023407203,-0.0061059577
C,0,-0.0105382234,-0.0009828502,1.3960507696
C,0,1.1963293835,0.0008482289,2.0836565821
C,0,2.4017070323,0.0013874404,1.3848730615
C,0,2.3960329021,0.0000663876,-0.0083983863
C,0,1.1930583325,-0.0017973675,-0.7027897678
H,0,-0.9559508099,-0.0014000768,1.9332262841
H,0,1.1970309638,0.0018833645,3.1710047059
H,0,3.3448401376,0.0028403362,1.9257236886
H,0,3.3348610549,0.0004888979,-0.5569642211
H,0,1.1792286438,-0.0028298871,-1.7900693006
C,0,-1.2626858738,-0.0042066061,-0.7165897895
C,0,-2.3133333515,-0.0056866308,-1.318032676
H,0,-3.2391975791,-0.0072765166,-1.8484039929

*b1b95/6-31+g***
E(RB1B95) = -308.267306580

Zero-point correction= 0.110295 (Hartree/Particle)
Thermal correction to Energy= 0.116722
Thermal correction to Enthalpy= 0.117667
Thermal correction to Gibbs Free Energy= 0.079880
Sum of electronic and ZPE= -308.157011
Sum of electronic and thermal Energies= -308.150584
Sum of electronic and thermal Enthalpies= -308.149640
Sum of electronic and thermal Free Energies= -308.187427

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 73.244 25.141 79.529

C,0,-0.0231117154,0.,-0.0076565644
C,0,-0.0101847346,0.,1.3933313241
C,0,1.1954633553,0.,2.0806307749
C,0,2.4000448977,0.,1.3841986605
C,0,2.3947061341,0.,-0.0072033984

C,0,1.1935667141,0.,-0.7023576307
H,0,-0.9503798082,0.,1.9309410111
H,0,1.19442364,0.,3.1644328412
H,0,3.3398218178,0.,1.9240001598
H,0,3.3303699761,0.,-0.5541599413
H,0,1.1842572214,0.,-1.7853648422
C,0,-1.2603978952,0.,-0.7183184101
C,0,-2.3091733676,0.,-1.3207879571
H,0,-3.2326232355,0.,-1.8511280276

*PBEh1PBE/6-31+g***
E(RPBEh1PBE) = -308.070683237

Zero-point correction= 0.110299 (Hartree/Particle)
Thermal correction to Energy= 0.116705
Thermal correction to Enthalpy= 0.117650
Thermal correction to Gibbs Free Energy= 0.079903
Sum of electronic and ZPE= -307.960384
Sum of electronic and thermal Energies= -307.953978
Sum of electronic and thermal Enthalpies= -307.953034
Sum of electronic and thermal Free Energies= -307.990780

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 73.234 25.088 79.443

C,0,-0.0246034068,0.,-0.0085262199
C,0,-0.0117102575,0.,1.3951638068
C,0,1.1959665137,0.,2.0836802913
C,0,2.4028408708,0.,1.3858006157
C,0,2.3976080685,0.,-0.0083115572
C,0,1.194400182,0.,-0.7046108053
H,0,-0.9541395904,0.,1.9334916137
H,0,1.1950938902,0.,3.1697009043
H,0,3.3445322869,0.,1.926706058
H,0,3.3352751348,0.,-0.5562373339
H,0,1.1845865493,0.,-1.789909559
C,0,-1.2625566639,0.,-0.7195878104
C,0,-2.3127253221,0.,-1.3227957176
H,0,-3.2377852554,0.,-1.8540062866

*b972/6-31+g***
E(RB972) = -308.302673520

Zero-point correction= 0.110169 (Hartree/Particle)
Thermal correction to Energy= 0.116599
Thermal correction to Enthalpy= 0.117543
Thermal correction to Gibbs Free Energy= 0.079755
Sum of electronic and ZPE= -308.192505
Sum of electronic and thermal Energies= -308.186075

Sum of electronic and thermal Enthalpies= -308.185130
Sum of electronic and thermal Free Energies= -308.222918

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 73.167 25.183 79.532

C,0,-0.0259736263,0.,-0.0093088207
C,0,-0.0122074049,0.,1.396087927
C,0,1.1965592781,0.,2.0850401156
C,0,2.4045762995,0.,1.3867950367
C,0,2.3990782122,0.,-0.0084883027
C,0,1.1949417991,0.,-0.7055039485
H,0,-0.9522916408,0.,1.9347572108
H,0,1.1954984777,0.,3.1693244492
H,0,3.3447535611,0.,1.9268290909
H,0,3.3351481728,0.,-0.5557060961
H,0,1.1865994604,0.,-1.7889490006
C,0,-1.2649440793,0.,-0.7209575554
C,0,-2.3157933356,0.,-1.3245553886
H,0,-3.2391621741,0.,-1.8548067177

*b3p86/6-31+g***
E(RB3P86) = -309.378632400

Zero-point correction= 0.109829 (Hartree/Particle)
Thermal correction to Energy= 0.116264
Thermal correction to Enthalpy= 0.117208
Thermal correction to Gibbs Free Energy= 0.079421
Sum of electronic and ZPE= -309.268804
Sum of electronic and thermal Energies= -309.262369
Sum of electronic and thermal Enthalpies= -309.261424
Sum of electronic and thermal Free Energies= -309.299212

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 72.957 25.237 79.531

C,0,-0.0254907204,0.,-0.0090367673
C,0,-0.0120598476,0.,1.395567488
C,0,1.1959741911,0.,2.084086771
C,0,2.4033244676,0.,1.3860851549
C,0,2.3979644059,0.,-0.0084998053
C,0,1.1945774498,0.,-0.7051116617
H,0,-0.954080233,0.,1.9339935478
H,0,1.1950349572,0.,3.1698537471
H,0,3.3447798197,0.,1.9268588338
H,0,3.3353813875,0.,-0.5563508504
H,0,1.1850593279,0.,-1.7901066989
C,0,-1.2624720199,0.,-0.7195479925

C,0,-2.3132852329,0.,-1.3231297601
H,0,-3.2379249528,0.,-1.8541040063

*b3pw91/6-31+g***
E(RB3PW91) = -308.290083192

Zero-point correction= 0.109671 (Hartree/Particle)
Thermal correction to Energy= 0.116115
Thermal correction to Enthalpy= 0.117059
Thermal correction to Gibbs Free Energy= 0.079253
Sum of electronic and ZPE= -308.180412
Sum of electronic and thermal Energies= -308.173968
Sum of electronic and thermal Enthalpies= -308.173024
Sum of electronic and thermal Free Energies= -308.210831

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 72.863 25.270 79.571

C,0,-0.0263857611,0.,-0.0095473932
C,0,-0.012588078,0.,1.3965502483
C,0,1.1966675744,0.,2.0857249584
C,0,2.4052408206,0.,1.3871732716
C,0,2.3997257381,0.,-0.0087451994
C,0,1.1951502301,0.,-0.7060700421
H,0,-0.9547404422,0.,1.935907789
H,0,1.1956208631,0.,3.1721529197
H,0,3.3472680121,0.,1.9282690197
H,0,3.3376541309,0.,-0.5570313766
H,0,1.1863593465,0.,-1.7916482989
C,0,-1.2649539669,0.,-0.7209620227
C,0,-2.3165235686,0.,-1.3249714726
H,0,-3.2417118991,0.,-1.8562444012

*b3lyp/6-31+g***
E(RB3LYP) = -308.417619878

Zero-point correction= 0.109362 (Hartree/Particle)
Thermal correction to Energy= 0.115808
Thermal correction to Enthalpy= 0.116752
Thermal correction to Gibbs Free Energy= 0.078947
Sum of electronic and ZPE= -308.308258
Sum of electronic and thermal Energies= -308.301812
Sum of electronic and thermal Enthalpies= -308.300868
Sum of electronic and thermal Free Energies= -308.338673

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 72.670 25.313 79.566

C,0,-0.0283723095,0.,-0.0109611533
C,0,-0.0136575877,0.,1.3978024495
C,0,1.1974990116,0.,2.0883853579
C,0,2.4083327814,0.,1.3890082304
C,0,2.402652253,0.,-0.0092864893
C,0,1.1960533997,0.,-0.7077965214
H,0,-0.9551306683,0.,1.9374250562
H,0,1.1962189034,0.,3.1744268326
H,0,3.3499687881,0.,1.929999538
H,0,3.3402293797,0.,-0.5574061244
H,0,1.1880376461,0.,-1.7929227613
C,0,-1.2691144048,0.,-0.7238411593
C,0,-2.3211133494,0.,-1.3265212484
H,0,-3.2448208433,0.,-1.857754007

*b3lyp/6-31+g** with PCM solvent model*
scrf=(solvent=1-propanol)
E(RB3LYP) = -308.421768879

Zero-point correction= 0.109314 (Hartree/Particle)
Thermal correction to Energy= 0.115750
Thermal correction to Enthalpy= 0.116694
Thermal correction to Gibbs Free Energy= 0.078897
Sum of electronic and ZPE= -308.312455
Sum of electronic and thermal Energies= -308.306019
Sum of electronic and thermal Enthalpies= -308.305075
Sum of electronic and thermal Free Energies= -308.342872

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 72.634 25.272 79.552

C,0,-0.0278877495,0.,-0.0105036538
C,0,-0.0147318118,0.,1.3990641065
C,0,1.1972765605,0.,2.0897662703
C,0,2.4085511684,0.,1.3893830394
C,0,2.4036044878,0.,-0.0097927921
C,0,1.1964957259,0.,-0.7090247428
H,0,-0.9547522062,0.,1.9414919379
H,0,1.1959178912,0.,3.1756217279
H,0,3.3500425854,0.,1.9303271827
H,0,3.3410167189,0.,-0.5578281782
H,0,1.1916998465,0.,-1.7943096424
C,0,-1.2699245629,0.,-0.7241199024
C,0,-2.3223321738,0.,-1.3288156295
H,0,-3.2481934804,0.,-1.8607017233

<u>Transition States for the major product for the reaction of phenylacetylene</u>
*m062x/6-31+g***
E(RM062X) = -439.912920619

Zero-point correction= 0.152028 (Hartree/Particle)
Thermal correction to Energy= 0.160766
Thermal correction to Enthalpy= 0.161711
Thermal correction to Gibbs Free Energy= 0.117188
Sum of electronic and ZPE= -439.760892
Sum of electronic and thermal Energies= -439.752154
Sum of electronic and thermal Enthalpies= -439.751210
Sum of electronic and thermal Free Energies= -439.795733

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 100.882 33.375 93.707

C,0,1.1550388923,0.2598123157,-0.6249715359
C,0,-0.0641855727,0.1591024317,0.0602900388
C,0,-0.0539358846,-0.1595664462,1.4247405042
C,0,1.1518262265,-0.3756874061,2.0872853185
C,0,2.3596445831,-0.2725911768,1.398863898
C,0,2.3581769249,0.0428772641,0.0402706767
C,0,-1.3305176939,0.3735524768,-0.6258113916
C,0,-2.4709057529,0.03974906,-1.0496387143
H,0,-0.9987060023,-0.2380566874,1.9538444078
H,0,1.1479354382,-0.6236159105,3.1441971892
H,0,3.2980910758,-0.4409611189,1.9175222266
H,0,3.2949645757,0.1125357232,-0.5039372803
H,0,1.1518563589,0.4817310881,-1.6889878355
H,0,-3.0597529128,-0.8609612506,-1.0759324769
N,0,-1.2192478409,2.2570720494,-1.1079798115
O,0,-2.4125614012,2.4757434977,-1.7120298373
H,0,-1.1275431769,2.8220892185,-0.2648921348
H,0,-2.8145434623,1.4776212324,-1.6180167605
H,0,-0.450521375,2.442330639,-1.7500194812

*m06/6-31+g***
E(RM06) = -439.798170029

Zero-point correction= 0.149473 (Hartree/Particle)
Thermal correction to Energy= 0.158274
Thermal correction to Enthalpy= 0.159219
Thermal correction to Gibbs Free Energy= 0.114826
Sum of electronic and ZPE= -439.648697
Sum of electronic and thermal Energies= -439.639896
Sum of electronic and thermal Enthalpies= -439.638951
Sum of electronic and thermal Free Energies= -439.683344

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 99.319 33.922 93.431

C,0,1.1927444671,-0.1851181845,-0.7233410547
C,0,0.0058064652,0.1406199604,-0.0524170688
C,0,0.0318759407,0.276688767,1.3434330096
C,0,1.2143610096,0.0885656609,2.0489429058
C,0,2.3892326623,-0.2345833874,1.3722825788
C,0,2.3739007741,-0.3725403045,-0.0136402529
C,0,-1.2185613318,0.3276027264,-0.7964792919
C,0,-2.1949777081,0.0056796135,-1.5312212131
H,0,-0.8919078917,0.5093979694,1.8711782166
H,0,1.2184283629,0.1875696341,3.1319419921
H,0,3.3140707944,-0.3812874194,1.9249256137
H,0,3.2875279009,-0.6268314881,-0.5458283286
H,0,1.1723297398,-0.2925167738,-1.8057615184
H,0,-2.5787057996,-0.9048598581,-1.9641531487
N,0,-1.5351744256,2.2803126847,-0.6125449118
O,0,-2.6514774657,2.4439138436,-1.3473790573
H,0,-1.6866622747,2.5426814484,0.3617196102
H,0,-2.7821675008,1.3745715599,-1.6503682762
H,0,-0.7455307189,2.7929105476,-1.0064928045

*b1b95/6-31+g***
E(RB1B95) = -439.912443216

Zero-point correction= 0.150427 (Hartree/Particle)
Thermal correction to Energy= 0.159363
Thermal correction to Enthalpy= 0.160307
Thermal correction to Gibbs Free Energy= 0.115348
Sum of electronic and ZPE= -439.762016
Sum of electronic and thermal Energies= -439.753080
Sum of electronic and thermal Enthalpies= -439.752136
Sum of electronic and thermal Free Energies= -439.797095

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 100.002 34.006 94.624

C,0,1.1580460916,0.2323833239,-0.627799539
C,0,-0.055233382,0.1502227543,0.0686853349
C,0,-0.0280970651,-0.1239194192,1.4420404637
C,0,1.1814769246,-0.3150617511,2.0976292718
C,0,2.3803209076,-0.2318902613,1.3967310177
C,0,2.3643647153,0.0404751664,0.0319779321
C,0,-1.3163554461,0.332732244,-0.609033579
C,0,-2.4533187509,0.0097067808,-1.0485184628
H,0,-0.96428832,-0.1894618579,1.9834529351
H,0,1.1873228601,-0.5291972683,3.1602111752
H,0,3.3226686619,-0.3816001948,1.9106016957
H,0,3.2946870733,0.0972532199,-0.5214415296
H,0,1.145824886,0.4237626132,-1.6952306796
H,0,-3.0465208737,-0.8865319626,-1.0942332106

N,0,-1.2690510508,2.2657362833,-1.1221358424
O,0,-2.4678445349,2.4113264783,-1.7180665775
H,0,-1.1935044421,2.8415645883,-0.2883832939
H,0,-2.8176743036,1.3662170809,-1.5953148058
H,0,-0.5077129512,2.4590601818,-1.766380306

*PBEh1PBE/6-31+g***
E(RPBEh1PBE) = -439.645315811

Zero-point correction= 0.150448 (Hartree/Particle)
Thermal correction to Energy= 0.159375
Thermal correction to Enthalpy= 0.160319
Thermal correction to Gibbs Free Energy= 0.114846
Sum of electronic and ZPE= -439.494868
Sum of electronic and thermal Energies= -439.485941
Sum of electronic and thermal Enthalpies= -439.484997
Sum of electronic and thermal Free Energies= -439.530470

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 100.009 33.955 95.705

C,0,-0.9860790783,1.1953566634,0.3833429626
C,0,-0.2747988731,-0.0148640315,0.370759676
C,0,-0.9453100282,-1.1922508438,0.0020611916
C,0,-2.2931774774,-1.1577883421,-0.3396569843
C,0,-2.9911387908,0.0492364944,-0.3238159505
C,0,-2.3341564269,1.2235377882,0.0406002528
C,0,1.1203708696,-0.0445940864,0.7329132444
C,0,2.14173897,-0.0705071664,1.4707339003
H,0,-0.4024495469,-2.1331730749,0.0031751981
H,0,-2.8020187194,-2.0770661866,-0.6150226165
H,0,-4.0435867797,0.0736288028,-0.5904255901
H,0,-2.8743335616,2.1656674941,0.0601688341
H,0,-0.4722802241,2.1065966861,0.6747500251
H,0,2.3570936404,-0.1113576058,2.5256552419
N,0,2.0404163927,0.010730827,-1.0941326955
O,0,3.3320555388,-0.0030439854,-0.7184048697
H,0,1.7987985999,-0.8099680692,-1.6445661155
H,0,3.1673667302,-0.0384785384,0.3836279062
H,0,1.7993117649,0.8677231744,-1.5864036112

*b972/6-31+g***
E(RB972) = -439.956135240

Zero-point correction= 0.149905 (Hartree/Particle)
Thermal correction to Energy= 0.158882
Thermal correction to Enthalpy= 0.159827
Thermal correction to Gibbs Free Energy= 0.114568
Sum of electronic and ZPE= -439.806230

Sum of electronic and thermal Energies= -439.797253
Sum of electronic and thermal Enthalpies= -439.796309
Sum of electronic and thermal Free Energies= -439.841568

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 99.700 34.197 95.255

C,0,-0.9757322399,1.1914370467,0.3278975933
C,0,-0.2803347341,-0.0300646914,0.3640406586
C,0,-0.9717959974,-1.212983198,0.0484106864
C,0,-2.3220459512,-1.1728050306,-0.2879143711
C,0,-3.0031029326,0.0447411269,-0.3199028384
C,0,-2.3261904645,1.2246020165,-0.0088858565
C,0,1.1151503722,-0.0694936341,0.7239112607
C,0,2.1406835695,-0.1378623126,1.457434921
H,0,-0.4441818421,-2.1594706652,0.08424028
H,0,-2.8444755313,-2.0938347024,-0.5219923439
H,0,-4.0549284848,0.0734978414,-0.5813561402
H,0,-2.8517826858,2.173027317,-0.0255166328
H,0,-0.450596936,2.106194416,0.5785570678
H,0,2.3420981288,-0.2323994178,2.5104355358
N,0,2.0735497557,0.0835467983,-1.0968652131
O,0,3.3547170498,0.0437097632,-0.6968087655
H,0,1.8370237723,-0.704822704,-1.6913299304
H,0,3.1560915933,-0.0518372501,0.4178183621
H,0,1.8436775581,0.9642012803,-1.5468152737

*b3p86/6-31+g***
E(RB3P86) = -441.407429250

Zero-point correction= 0.149505 (Hartree/Particle)
Thermal correction to Energy= 0.158479
Thermal correction to Enthalpy= 0.159423
Thermal correction to Gibbs Free Energy= 0.114069
Sum of electronic and ZPE= -441.257924
Sum of electronic and thermal Energies= -441.248950
Sum of electronic and thermal Enthalpies= -441.248006
Sum of electronic and thermal Free Energies= -441.293361

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 99.447 34.230 95.457

C,0,1.1962454243,-0.0709448084,-0.7058125391
C,0,-0.0117836733,0.1110352304,-0.0119247593
C,0,0.0082829237,0.1232739095,1.3931416118
C,0,1.204937833,-0.045696332,2.0821704145
C,0,2.3990451255,-0.2252952409,1.3839019413
C,0,2.3896587693,-0.2396299261,-0.0105893118

C,0,-1.2469101562,0.2772106869,-0.7310427579
C,0,-2.2928017211,-0.0220788636,-1.3674233243
H,0,-0.9242986717,0.2513924355,1.9344455438
H,0,1.2051398692,-0.0414429133,3.168094818
H,0,3.3314925865,-0.3573627073,1.9241011524
H,0,3.3153160173,-0.3851828583,-0.5593991213
H,0,1.1838209472,-0.0888590802,-1.7911917167
H,0,-2.7954775017,-0.9190163975,-1.6892867301
N,0,-1.4497688844,2.3400069968,-0.7858552514
O,0,-2.6029090759,2.4430090803,-1.4759710405
H,0,-1.5367643852,2.7199681932,0.1545716619
H,0,-2.787723977,1.3393499398,-1.6213548623
H,0,-0.6703904497,2.7630406553,-1.2857837289

*b3pw91/6-31+g***
E(RB3PW91) = -439.944545312

Zero-point correction= 0.149166 (Hartree/Particle)
Thermal correction to Energy= 0.158173
Thermal correction to Enthalpy= 0.159117
Thermal correction to Gibbs Free Energy= 0.113486
Sum of electronic and ZPE= -439.795380
Sum of electronic and thermal Energies= -439.786373
Sum of electronic and thermal Enthalpies= -439.785428
Sum of electronic and thermal Free Energies= -439.831060

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 99.255 34.325 96.039

C,0,1.189365,0.042381,-0.68006
C,0,-0.028115,0.114474,0.021156
C,0,-0.009923,0.011437,1.423837
C,0,1.193407,-0.163097,2.103021
C,0,2.396067,-0.23295,1.397741
C,0,2.389006,-0.131898,0.005213
C,0,-1.273868,0.285071,-0.682092
C,0,-2.364,-0.013214,-1.243455
H,0,-0.947972,0.058416,1.969405
H,0,1.191954,-0.247342,3.186329
H,0,3.333337,-0.369417,1.929765
H,0,3.321227,-0.193172,-0.549674
H,0,1.180957,0.10956,-1.764362
H,0,-2.91928,-0.910155,-1.46632
N,0,-1.377459,2.345129,-0.93187
O,0,-2.556522,2.44268,-1.576951
H,0,-1.398996,2.813267,-0.027975
H,0,-2.800674,1.333725,-1.605439
H,0,-0.603398,2.677884,-1.503474

*b3lyp/6-31+g***
E(RB3LYP) = -440.118375115

Zero-point correction= 0.148084 (Hartree/Particle)
Thermal correction to Energy= 0.157155
Thermal correction to Enthalpy= 0.158100
Thermal correction to Gibbs Free Energy= 0.112804
Sum of electronic and ZPE= -439.970291
Sum of electronic and thermal Energies= -439.961220
Sum of electronic and thermal Enthalpies= -439.960276
Sum of electronic and thermal Free Energies= -440.005571

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 98.617 34.633 95.333

C,0,1.199063485,0.0054372887,-0.687687451
C,0,-0.0186938342,0.1173525685,0.0136078878
C,0,0.0004849281,0.0478052288,1.4214174171
C,0,1.2033451853,-0.1333023341,2.1042023892
C,0,2.4055462536,-0.2432757684,1.3982456385
C,0,2.3982953811,-0.1749830823,0.0013766667
C,0,-1.2614491927,0.2932930918,-0.6960382021
C,0,-2.3404534192,-0.0029626061,-1.2863374889
H,0,-0.9345768979,0.1251011918,1.9678907625
H,0,1.2018962552,-0.1918951991,3.1888329971
H,0,3.3404419008,-0.3845458229,1.9324458068
H,0,3.3280729328,-0.2662063512,-0.5527273975
H,0,1.1910165533,0.0484313393,-1.7726533159
H,0,-2.8579270991,-0.9172024589,-1.5318189928
N,0,-1.4204486496,2.3651181935,-0.8949962909
O,0,-2.5980187974,2.4491501968,-1.5593673164
H,0,-1.4672724761,2.8093434313,0.0215279705
H,0,-2.8093417494,1.2946461706,-1.6169298773
H,0,-0.6448697596,2.7314729218,-1.4461992031

*b3lyp/6-31+g** with PCM solvent model*
E(RB3LYP) = -440.128482594
Scrf=(solvent=1-propanol)

Zero-point correction= 0.147921 (Hartree/Particle)
Thermal correction to Energy= 0.157065
Thermal correction to Enthalpy= 0.158009
Thermal correction to Gibbs Free Energy= 0.111945
Sum of electronic and ZPE= -439.980562
Sum of electronic and thermal Energies= -439.971417
Sum of electronic and thermal Enthalpies= -439.970473
Sum of electronic and thermal Free Energies= -440.016537

E CV S

KCal/Mol Cal/Mol-K Cal/Mol-K
Total 98.560 34.786 96.950

C,0,1.1979972282,0.0084091637,-0.6876923913
C,0,-0.018518397,0.1139242809,0.0167257129
C,0,-0.0017478285,0.0412962312,1.4244445883
C,0,1.2022543591,-0.1397876671,2.1064405578
C,0,2.4045274412,-0.2462028926,1.3985040985
C,0,2.3979855981,-0.1722112024,0.0010780535
C,0,-1.2639418998,0.2786715413,-0.6923354324
C,0,-2.3448300587,-0.020166945,-1.2755680291
H,0,-0.934794237,0.1228103935,1.9733752433
H,0,1.2017349976,-0.1985999035,3.1908356314
H,0,3.3398689732,-0.3864752251,1.9319965504
H,0,3.3280813051,-0.2565563856,-0.5531356743
H,0,1.1925548194,0.0637804809,-1.7719158431
H,0,-2.8684854456,-0.9333998153,-1.5141473868
N,0,-1.4090746572,2.3694467543,-0.90256899
O,0,-2.598851929,2.4449976639,-1.5688866116
H,0,-1.4595078357,2.8289712185,0.0053001062
H,0,-2.8071805055,1.3141478595,-1.6147408101
H,0,-0.6429599279,2.7397204491,-1.4629153736

<u>*p*-chlorophenylacetylene</u>
*m062x/6-31+g***
E(RM062X) = -767.842686748

Zero-point correction= 0.100994 (Hartree/Particle)
Thermal correction to Energy= 0.108501
Thermal correction to Enthalpy= 0.109445
Thermal correction to Gibbs Free Energy= 0.068432
Sum of electronic and ZPE= -767.741693
Sum of electronic and thermal Energies= -767.734186
Sum of electronic and thermal Enthalpies= -767.733242
Sum of electronic and thermal Free Energies= -767.774254

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 68.085 28.607 86.319

C,0,0.0218889263,-0.0019471893,-0.1568938398
C,0,-0.0510145065,-0.0011935608,1.2428328737
C,0,1.1079457684,0.0003556245,2.0100800942
C,0,2.3450623024,0.0010797928,1.3718950499
C,0,2.4417405984,0.0003031499,-0.0167089618
C,0,1.2785214897,-0.001243731,-0.7775889397
H,0,-1.0227428388,-0.0017551792,1.7251016364
H,0,1.0579556285,0.0009853126,3.093287953
Cl,0,3.8008207207,0.0029321971,2.3299586599
H,0,3.4167453344,0.0008941785,-0.4912657701

H,0,1.3370891384,-0.0018435662,-1.8608290578
C,0,-1.1771085108,-0.0033588551,-0.945862579
C,0,-2.1862058386,-0.0061608333,-1.6098373182
H,0,-3.0775912125,-0.0080533404,-2.1964018007

*m06/6-31+g***
E(RM06) = -767.735248154

Zero-point correction= 0.099597 (Hartree/Particle)
Thermal correction to Energy= 0.107197
Thermal correction to Enthalpy= 0.108141
Thermal correction to Gibbs Free Energy= 0.066984
Sum of electronic and ZPE= -767.635651
Sum of electronic and thermal Energies= -767.628051
Sum of electronic and thermal Enthalpies= -767.627107
Sum of electronic and thermal Free Energies= -767.668265

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 67.267 29.075 86.623

C,0,0.0200519472,-0.0020715877,-0.1582851684
C,0,-0.0503957913,-0.0014622397,1.2420723765
C,0,1.1064648218,0.0001458434,2.0087506634
C,0,2.3426071377,0.0011096548,1.3705714346
C,0,2.4400510466,0.0004991293,-0.0170874525
C,0,1.2783884716,-0.00111065,-0.7765988261
H,0,-1.0245245449,-0.002219502,1.7246162423
H,0,1.0567024587,0.0006549558,3.0942175104
Cl,0,3.8003600181,0.0031153993,2.3302575865
H,0,3.4173392897,0.0012802458,-0.4920854444
H,0,1.3366289315,-0.0015943994,-1.8621330806
C,0,-1.1721797631,-0.0036262933,-0.9429378025
C,0,-2.1833165632,-0.005921739,-1.608410582
H,0,-3.0750704604,-0.0078048172,-2.1951794573

*b1b95/6-31+g***
E(RB1B95) = -767.910792651

Zero-point correction= 0.100705 (Hartree/Particle)
Thermal correction to Energy= 0.108291
Thermal correction to Enthalpy= 0.109235
Thermal correction to Gibbs Free Energy= 0.068091
Sum of electronic and ZPE= -767.810088
Sum of electronic and thermal Energies= -767.802502
Sum of electronic and thermal Enthalpies= -767.801558
Sum of electronic and thermal Free Energies= -767.842702

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K

Total 67.954 28.916 86.596

C,0,-0.0666232296,-0.002260509,-0.0331282313
C,0,-0.0505422932,-0.0027926115,1.3673255645
C,0,1.1496032571,-0.001180619,2.0615064925
C,0,2.3456399835,0.0009911497,1.353742952
C,0,2.3555018598,0.0015683269,-0.0359774347
C,0,1.1517325765,-0.0000550883,-0.7238642506
H,0,-0.9876273156,-0.0044888295,1.9097976396
H,0,1.1610071333,-0.0015976162,3.143861115
Cl,0,3.8506178611,0.003022847,2.2189949092
H,0,3.2966031652,0.0032708007,-0.5707186105
H,0,1.1490493333,0.0003782229,-1.8066296122
C,0,-1.3026486888,-0.0039319342,-0.7436304961
C,0,-2.3512589683,-0.0053266537,-1.3459950434
H,0,-3.2748646743,-0.0066614859,-1.876357994

*pbeh1pbe/6-31+g***
E(RPBEh1PBE) = -767.525647581

Zero-point correction= 0.100726 (Hartree/Particle)
Thermal correction to Energy= 0.108291
Thermal correction to Enthalpy= 0.109235
Thermal correction to Gibbs Free Energy= 0.068121
Sum of electronic and ZPE= -767.424921
Sum of electronic and thermal Energies= -767.417356
Sum of electronic and thermal Enthalpies= -767.416412
Sum of electronic and thermal Free Energies= -767.457526

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 67.954 28.852 86.532

C,0,0.018174723,-0.0022155187,-0.1594300884
C,0,-0.0503675706,-0.001515952,1.2421839414
C,0,1.107719761,0.0001926608,2.0087247018
C,0,2.3468111037,0.0011826153,1.3733278293
C,0,2.4404594856,0.0004882986,-0.0159939928
C,0,1.2784318163,-0.0012210723,-0.7765946885
H,0,-1.0207026085,-0.0022903118,1.7278342833
H,0,1.0536047176,0.0007561638,3.0920739593
Cl,0,3.7980832203,0.0033037375,2.3286383148
H,0,3.4140812398,0.0012797591,-0.494149875
H,0,1.3408621705,-0.0017662553,-1.8598809166
C,0,-1.1733236421,-0.0039141627,-0.9437108407
C,0,-2.1847336465,-0.0059075783,-1.6094439647
H,0,-3.0759937702,-0.007378384,-2.1958106631

*b972/6-31+g***
E(RB972) = -767.920774939

Zero-point correction= 0.100573 (Hartree/Particle)
Thermal correction to Energy= 0.108165
Thermal correction to Enthalpy= 0.109109
Thermal correction to Gibbs Free Energy= 0.067946
Sum of electronic and ZPE= -767.820202
Sum of electronic and thermal Energies= -767.812610
Sum of electronic and thermal Enthalpies= -767.811666
Sum of electronic and thermal Free Energies= -767.852829

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 67.875 28.962 86.635

C,0,0.0167151861,-0.0025081465,-0.1606069305
C,0,-0.050916791,-0.0016616328,1.2427631718
C,0,1.1079811797,0.0002121663,2.0100206196
C,0,2.348883369,0.0012928038,1.3747872777
C,0,2.4418993449,0.0005158799,-0.0160204685
C,0,1.2789389189,-0.001360372,-0.7773447014
H,0,-1.0188284229,-0.0025166979,1.7290544045
H,0,1.0522138503,0.0008346527,3.0913620259
Cl,0,3.8011089177,0.0036555305,2.3310620952
H,0,3.4130145768,0.0013713822,-0.4949072077
H,0,1.3433285749,-0.0019811105,-1.85862747
C,0,-1.1757705667,-0.0044843447,-0.9453593243
C,0,-2.1879900658,-0.0056367542,-1.6114404364
H,0,-3.0774710718,-0.0067393567,-2.196975056

*b3p86/6-31+g***
E(RB3LYP) = -768.011546262

Zero-point correction= 0.099767 (Hartree/Particle)
Thermal correction to Energy= 0.107392
Thermal correction to Enthalpy= 0.108336
Thermal correction to Gibbs Free Energy= 0.067118
Sum of electronic and ZPE= -767.911780
Sum of electronic and thermal Energies= -767.904155
Sum of electronic and thermal Enthalpies= -767.903210
Sum of electronic and thermal Free Energies= -767.944428

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 67.389 29.128 86.750

C,0,0.0138337281,-0.002059371,-0.162276772
C,0,-0.0534445702,-0.0013725964,1.2443795499
C,0,1.1082531987,0.0002468359,2.013358456
C,0,2.3500292028,0.0011178143,1.3754337174
C,0,2.4449228529,0.0003960963,-0.0173284453

C,0,1.2791957224,-0.0012268841,-0.7802793647
H,0,-1.0228651877,-0.0020427787,1.7315520269
H,0,1.0525406457,0.0008285791,3.0963756931
Cl,0,3.8171653501,0.0031309231,2.3412095949
H,0,3.4175939762,0.0010917919,-0.4968503882
H,0,1.3434009678,-0.0017827611,-1.8633261859
C,0,-1.1805765863,-0.0036149856,-0.9484427354
C,0,-2.193163628,-0.0060884296,-1.614915428
H,0,-3.0837786726,-0.0076302342,-2.2011217187

*b3pw91/6-31+g***
E(RB3PW91) = -767.832464445

Zero-point correction= 0.100111 (Hartree/Particle)
Thermal correction to Energy= 0.107723
Thermal correction to Enthalpy= 0.108667
Thermal correction to Gibbs Free Energy= 0.067472
Sum of electronic and ZPE= -767.732353
Sum of electronic and thermal Energies= -767.724741
Sum of electronic and thermal Enthalpies= -767.723797
Sum of electronic and thermal Free Energies= -767.764992

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 67.597 29.056 86.702

C,0,0.0160552022,-0.0024731222,-0.1606597832
C,0,-0.0514231202,-0.0015872623,1.2434119549
C,0,1.108166067,0.0002644032,2.0106304727
C,0,2.349184417,0.0012773627,1.3746562941
C,0,2.442356336,0.0004547869,-0.0166262357
C,0,1.2788630104,-0.0014012635,-0.7780964006
H,0,-1.0213649334,-0.00239039,1.7304385014
H,0,1.0531104962,0.0009231827,3.0942314318
Cl,0,3.8051101296,0.0036122705,2.333019763
H,0,3.415660881,0.0012602179,-0.4960965955
H,0,1.3425962519,-0.0020578487,-1.8615604266
C,0,-1.1760757693,-0.0044176968,-0.9452366806
C,0,-2.1888956785,-0.0056096128,-1.611946003
H,0,-3.0802362898,-0.0068610276,-2.1983982926

*b3lyp/6-31+g***
E(RB3LYP) = -768.011546262

Zero-point correction= 0.099766 (Hartree/Particle)
Thermal correction to Energy= 0.107391
Thermal correction to Enthalpy= 0.108335
Thermal correction to Gibbs Free Energy= 0.067118
Sum of electronic and ZPE= -767.911780
Sum of electronic and thermal Energies= -767.904155

Sum of electronic and thermal Enthalpies= -767.903211
Sum of electronic and thermal Free Energies= -767.944428

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 67.389 29.128 86.750

C,0,0.0138337776,-0.002059365,-0.1622768764
C,0,-0.0534445936,-0.0013725933,1.2443794536
C,0,1.1082531831,0.0002468357,2.0133584358
C,0,2.350029231,0.0011178134,1.3754337196
C,0,2.4449228957,0.0003960968,-0.0173284454
C,0,1.2791958161,-0.0012268798,-0.7802793725
H,0,-1.0228652393,-0.0020427771,1.7315519108
H,0,1.0525405934,0.0008285763,3.0963756905
Cl,0,3.8171653144,0.003130918,2.3412096795
H,0,3.4175940185,0.0010917903,-0.4968503518
H,0,1.3434010948,-0.0017827572,-1.8633261701
C,0,-1.1805765469,-0.0036149816,-0.9484428393
C,0,-2.1931636988,-0.006088433,-1.6149153549
H,0,-3.083778846,-0.0076302435,-2.2011214794

*b3lyp/6-31+g***
scrf=(solvent=1-propanol)
E(RB3LYP) = -768.015775699

Zero-point correction= 0.099688 (Hartree/Particle)
Thermal correction to Energy= 0.107316
Thermal correction to Enthalpy= 0.108260
Thermal correction to Gibbs Free Energy= 0.067024
Sum of electronic and ZPE= -767.916088
Sum of electronic and thermal Energies= -767.908460
Sum of electronic and thermal Enthalpies= -767.907515
Sum of electronic and thermal Free Energies= -767.948752

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 67.342 29.130 86.790

C,0,0.0150758142,-0.0020570408,-0.1614109482
C,0,-0.054254614,-0.0013824662,1.2456699748
C,0,1.1078233138,0.0002389379,2.0151408139
C,0,2.3476487012,0.001112685,1.3738007835
C,0,2.4463617457,0.0004026839,-0.0185337237
C,0,1.2799854556,-0.0012219739,-0.7815562274
H,0,-1.0219115403,-0.0020541103,1.7360598056
H,0,1.0488849946,0.000811706,3.0978343759
Cl,0,3.8187429495,0.0031333202,2.3421089601
H,0,3.4174303346,0.0011006553,-0.5009494032
H,0,1.3477598116,-0.0017678697,-1.8642599478

C,0,-1.1804822078,-0.0035980519,-0.9483049176
C,0,-2.1939917886,-0.0060794545,-1.6153716931
H,0,-3.08596597,-0.0076450209,-2.2024598527

Transition States for the major product for the reaction of *p*-chlorophenylacetylene
*m062x/6-31+g***
E(RM062X) = -899.481144765

Zero-point correction= 0.142225 (Hartree/Particle)
Thermal correction to Energy= 0.152170
Thermal correction to Enthalpy= 0.153114
Thermal correction to Gibbs Free Energy= 0.105134
Sum of electronic and ZPE= -899.338920
Sum of electronic and thermal Energies= -899.328975
Sum of electronic and thermal Enthalpies= -899.328030
Sum of electronic and thermal Free Energies= -899.376011

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.488 37.218 100.984

O,0,0.4061302597,-0.3111703153,-0.1172219789
H,0,0.5352599379,0.0041713505,0.907060969
C,0,1.6525798165,0.3581632396,1.9735100357
C,0,2.6101235552,0.1230697449,1.1867251088
N,0,1.7150451062,-0.4036552602,-0.4557185471
C,0,4.015594404,0.0792092233,0.8108858271
H,0,1.5344612739,0.6684960856,2.9974192831
H,0,1.9441147012,-1.3554072254,-0.7371867425
H,0,1.9462581591,0.2547184138,-1.1985893906
C,0,4.6219651467,-1.1122015241,0.3894872469
C,0,5.9688087775,-1.1456059868,0.0446963119
C,0,6.7170239845,0.025876411,0.1198937795
C,0,6.1406554385,1.2215444258,0.5382465983
C,0,4.7921809439,1.2432393733,0.8799305066
H,0,4.0407042096,-2.0296739261,0.3588476525
H,0,6.4399713492,-2.0699386285,-0.2714986948
Cl,0,8.4040922795,-0.0070449243,-0.3140994352
H,0,6.7423094434,2.1223818494,0.591754468
H,0,4.3287412134,2.1688016735,1.2064090018

*m06/6-31+g***
E(RM06) = -899.366677290

Zero-point correction= 0.139864 (Hartree/Particle)
Thermal correction to Energy= 0.149883
Thermal correction to Enthalpy= 0.150827
Thermal correction to Gibbs Free Energy= 0.103111
Sum of electronic and ZPE= -899.226813
Sum of electronic and thermal Energies= -899.216795

Sum of electronic and thermal Enthalpies= -899.215850
Sum of electronic and thermal Free Energies= -899.263566

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.053 37.816 100.427

O,0,0.4043113045,0.2334739664,-0.1160440303
H,0,0.5787085779,-0.0579289309,0.9449171026
C,0,1.6438096473,-0.3446411295,1.9639633609
C,0,2.6284634139,-0.1260084992,1.2030284106
N,0,1.6956846047,0.3477989034,-0.4815579624
C,0,4.0218115844,-0.0826678972,0.8252215726
H,0,1.4915439526,-0.621298581,2.9953049324
H,0,1.9408722972,-0.3257502528,-1.2081074247
H,0,1.9102563095,1.2977676515,-0.7853995637
C,0,4.8028403803,-1.2444042601,0.9027024627
C,0,6.1474818476,-1.2255212988,0.5532635089
C,0,6.7177219941,-0.0348186976,0.1166869661
C,0,5.9688010748,1.1347951248,0.03332256
C,0,4.6264409467,1.1044592274,0.3873997957
H,0,4.3408429452,-2.1682537279,1.2431947723
H,0,6.7519932832,-2.1264413853,0.6142236569
Cl,0,8.4045726242,-0.0043000796,-0.3326303903
H,0,6.4383141642,2.0569133624,-0.2981304755
H,0,4.0415490478,2.0218005039,0.3491927452
*b1b95/6-31+g***
E(RB1B95) = -899.555826372

Zero-point correction= 0.141070 (Hartree/Particle)
Thermal correction to Energy= 0.151143
Thermal correction to Enthalpy= 0.152087
Thermal correction to Gibbs Free Energy= 0.103678
Sum of electronic and ZPE= -899.414756
Sum of electronic and thermal Energies= -899.404683
Sum of electronic and thermal Enthalpies= -899.403739
Sum of electronic and thermal Free Energies= -899.452148

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.844 37.648 101.886

O,0,0.4022149834,-0.2478242536,-0.1222120798
H,0,0.5793810695,0.0017536929,0.9433657172
C,0,1.6458925757,0.2627631911,1.975882333
C,0,2.6318238523,0.0954036323,1.2073168915
N,0,1.6912441477,-0.3200248987,-0.5034923543
C,0,4.0237318977,0.0645535653,0.8299111292
H,0,1.4987184975,0.4900605194,3.0170715353
H,0,1.9265966876,-1.249474072,-0.8399947642

H,0,1.9140559347,0.3845716375,-1.2010874243
C,0,4.6503072814,-1.1340802168,0.4650256254
C,0,5.9917613835,-1.1610177828,0.1133972067
C,0,6.7203445284,0.0225667061,0.1208739926
C,0,6.124713732,1.2254777181,0.4800523148
C,0,4.7819246543,1.2416541845,0.8300659102
H,0,4.0840847822,-2.0584988235,0.4802648915
H,0,6.4738514246,-2.091348544,-0.1584131112
Cl,0,8.3989989222,-0.0040774076,-0.3230207595
H,0,6.7071639792,2.1379621891,0.483403946
H,0,4.3092096662,2.1745529628,1.112141

*pbeh1pbe/6-31+g***
E(RPBEh1PBE) = -899.100170588

Zero-point correction= 0.140961 (Hartree/Particle)
Thermal correction to Energy= 0.151050
Thermal correction to Enthalpy= 0.151994
Thermal correction to Gibbs Free Energy= 0.103388
Sum of electronic and ZPE= -898.959209
Sum of electronic and thermal Energies= -898.949121
Sum of electronic and thermal Enthalpies= -898.948176
Sum of electronic and thermal Free Energies= -898.996783

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.785 37.695 102.301

O,0,0.3967340314,0.1302061037,-0.1267670792
H,0,0.5898737215,-0.0307786099,0.956149194
C,0,1.649320155,-0.1918783421,2.0046650665
C,0,2.6456696969,-0.0796243528,1.2411460652
N,0,1.6774305965,0.1893055693,-0.534438558
C,0,4.0324430353,-0.0550569589,0.8496263834
H,0,1.4635910463,-0.3356690558,3.0561204967
H,0,1.9030302334,-0.5670724245,-1.1765250473
H,0,1.899113505,1.094420161,-0.9427638813
C,0,4.7759849079,-1.2439087403,0.7968381401
C,0,6.116846906,-1.2317157582,0.4302544081
C,0,6.7250877073,-0.0217185675,0.1076390946
C,0,6.0107213549,1.1729855022,0.1528141013
C,0,4.670995071,1.1509469608,0.520657984
H,0,4.294145915,-2.1821159827,1.0537712326
H,0,6.6889124794,-2.1527632744,0.3946345928
Cl,0,8.4000693889,-0.0003982578,-0.3549003055
H,0,6.5026535762,2.1082947299,-0.0920840558
H,0,4.1133966721,2.0815152981,0.5737141677

*b972/6-31+g***
E(RB972) = -899.574144944

Zero-point correction= 0.140300 (Hartree/Particle)
Thermal correction to Energy= 0.150458
Thermal correction to Enthalpy= 0.151402
Thermal correction to Gibbs Free Energy= 0.102667
Sum of electronic and ZPE= -899.433845
Sum of electronic and thermal Energies= -899.423687
Sum of electronic and thermal Enthalpies= -899.422743
Sum of electronic and thermal Free Energies= -899.471478

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.414 37.965 102.573

O,0,0.3806459226,-0.013715883,-0.137256368
H,0,0.6023785401,-0.0217065368,0.9773273178
C,0,1.6394917838,-0.0261330412,1.997061748
C,0,2.6480802571,-0.0164856805,1.2373462932
N,0,1.6520954442,-0.0054216516,-0.5670308282
C,0,4.0365902711,-0.010853523,0.8529568954
H,0,1.4608167084,-0.0337432131,3.0583898471
H,0,1.8762646119,-0.838183185,-1.1031210704
H,0,1.8691871209,0.8368561384,-1.0910654815
C,0,4.7410229789,-1.215600424,0.6864923787
C,0,6.0842772982,-1.2150165348,0.3253890896
C,0,6.7366386107,-0.0001100835,0.1217527223
C,0,6.0623686827,1.2096486151,0.2804076345
C,0,4.7193338309,1.1993803961,0.6417305132
H,0,4.2308776271,-2.1569760489,0.8548398248
H,0,6.6229326914,-2.146754321,0.2056755791
Cl,0,8.4157234998,0.0067083143,-0.3325742904
H,0,6.5843914533,2.1457799248,0.1261889988
H,0,4.1929026667,2.1373007377,0.776041196

*b3p86/6-31+g***
E(RB3LYP) = -899.712175619

Zero-point correction= 0.138430 (Hartree/Particle)
Thermal correction to Energy= 0.148720
Thermal correction to Enthalpy= 0.149664
Thermal correction to Gibbs Free Energy= 0.100821
Sum of electronic and ZPE= -899.573746
Sum of electronic and thermal Energies= -899.563456
Sum of electronic and thermal Enthalpies= -899.562512
Sum of electronic and thermal Free Energies= -899.611355

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 93.323 38.484 102.799

O,0,0.3534136101,-0.0092702922,-0.1344643919
H,0,0.6045263547,-0.0123941131,1.0139063622
C,0,1.6330736193,-0.0135143426,1.9890223758
C,0,2.6513900742,-0.0092669093,1.2384280563
N,0,1.6314280872,-0.004988419,-0.5815847031
C,0,4.0402558435,-0.0088669718,0.8545515902
H,0,1.4598734548,-0.0155439599,3.0538828879
H,0,1.8502658188,-0.8449763166,-1.1166968215
H,0,1.8460986999,0.8391176934,-1.1119238089
C,0,4.7440659193,-1.2192237983,0.695066594
C,0,6.090444493,-1.2235655896,0.3342791752
C,0,6.7456410207,-0.0085651723,0.1252085492
C,0,6.0744099997,1.2064010589,0.2760645624
C,0,4.7282445169,1.2016270956,0.6372035569
H,0,4.2304650847,-2.159897279,0.8673873109
H,0,6.6279727894,-2.1585607181,0.2196266816
Cl,0,8.4417560711,-0.0082070013,-0.3314903372
H,0,6.5998091516,2.1417546409,0.1167558302
H,0,4.2028853912,2.1429143944,0.7653285298

*b3pw91/6-31+g***
E(RB3PW91) = -899.486856399

Zero-point correction= 0.139568 (Hartree/Particle)
Thermal correction to Energy= 0.149758
Thermal correction to Enthalpy= 0.150702
Thermal correction to Gibbs Free Energy= 0.101886
Sum of electronic and ZPE= -899.347288
Sum of electronic and thermal Energies= -899.337098
Sum of electronic and thermal Enthalpies= -899.336154
Sum of electronic and thermal Free Energies= -899.384970

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 93.975 38.124 102.743

O,0,0.3792541305,-0.0415832894,-0.1324100669
H,0,0.6038388145,-0.0141522143,0.9818086368
C,0,1.6422350912,0.0152480177,2.005762268
C,0,2.6537143172,0.0022705326,1.2513782727
N,0,1.6534675848,-0.0458054159,-0.5687332557
C,0,4.0389840519,0.0011242472,0.8594623478
H,0,1.445321353,0.0378800307,3.0656312434
H,0,1.8758934808,-0.8975296477,-1.0806754771
H,0,1.8685944281,0.7835783574,-1.1190079016
C,0,4.7301163844,-1.2080529961,0.665150148
C,0,6.0715081317,-1.2140745092,0.295741574
C,0,6.7350588567,-0.0014036081,0.1126163278
C,0,6.0748910995,1.2124203533,0.2995295187
C,0,4.7333362851,1.2090257508,0.6688950146

H,0,4.2100977907,-2.1490115264,0.8188831534
H,0,6.6015301597,-2.1502101272,0.1539149954
Cl,0,8.4155753048,-0.0030620432,-0.3527492657
H,0,6.60728911,2.1476320267,0.1605275633
H,0,4.2153136255,2.150680061,0.8248269031

*b3lyp/6-31+g***
E(RB3LYP) = -899.712175644

Zero-point correction= 0.138427 (Hartree/Particle)
Thermal correction to Energy= 0.148717
Thermal correction to Enthalpy= 0.149662
Thermal correction to Gibbs Free Energy= 0.100826
Sum of electronic and ZPE= -899.573749
Sum of electronic and thermal Energies= -899.563458
Sum of electronic and thermal Enthalpies= -899.562514
Sum of electronic and thermal Free Energies= -899.611350

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 93.322 38.486 102.784

O,0,0.3534591659,-0.0143599878,-0.1356034926
H,0,0.6044168961,-0.0224434098,1.0129611792
C,0,1.6326879892,-0.0259462574,1.988292902
C,0,2.6513354465,-0.0161881255,1.2382410583
N,0,1.6315225453,-0.0055784459,-0.5825386588
C,0,4.0402263045,-0.010595156,0.8546361958
H,0,1.4591698868,-0.033588772,3.0530790307
H,0,1.8519628998,-0.8427300083,-1.1214251173
H,0,1.8445128185,0.8412977407,-1.1091277792
C,0,4.74683721,-1.2184627412,0.6887362357
C,0,6.0933288652,-1.2177565588,0.3283590139
C,0,6.7458190333,-0.0001335306,0.1261828478
C,0,6.0717676457,1.2124579605,0.2834526845
C,0,4.7255071828,1.2026443544,0.6441130933
H,0,4.2353227014,-2.1612348736,0.855714117
H,0,6.6330375398,-2.1508783547,0.2087945603
Cl,0,8.4420944662,0.0065988784,-0.3298664247
H,0,6.5950826404,2.1498627407,0.1294258484
H,0,4.1979287626,2.1420085468,0.777124706

*b3lyp/6-31+g** with PCM Solvent Model*
scrf=(solvent=1-propanol)
E(RB3LYP) = -899.722641877

Zero-point correction= 0.138375 (Hartree/Particle)
Thermal correction to Energy= 0.148707
Thermal correction to Enthalpy= 0.149651
Thermal correction to Gibbs Free Energy= 0.100510

Sum of electronic and ZPE= -899.584267
Sum of electronic and thermal Energies= -899.573935
Sum of electronic and thermal Enthalpies= -899.572991
Sum of electronic and thermal Free Energies= -899.622132

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 93.315 38.606 103.425

O,0,0.3528506993,-0.0696587867,-0.1291246626
H,0,0.5969106202,0.0008101837,0.9887798883
C,0,1.6422309442,0.0655273489,2.0039038279
C,0,2.6551606191,0.0191082802,1.2497078279
N,0,1.6399866747,-0.0992463516,-0.5838980051
C,0,4.0423207047,0.0108571576,0.8547498145
H,0,1.4681617498,0.1267417801,3.0673119046
H,0,1.8438225512,-0.9727727907,-1.0671959775
H,0,1.8462476813,0.7065572267,-1.1723130726
C,0,4.721576136,-1.2032220083,0.6324513593
C,0,6.0682867178,-1.2127511041,0.2720608563
C,0,6.7414747386,0.001840171,0.1294118199
C,0,6.0952854549,1.2207250437,0.340989547
C,0,4.7479892056,1.220320878,0.7005645965
H,0,4.1922413827,-2.1434832086,0.7480511873
H,0,6.5864367017,-2.1508637027,0.1069498998
Cl,0,8.4431448837,-0.0042843653,-0.3276121495
H,0,6.6336538619,2.1552111983,0.228104702
H,0,4.2382386727,2.1635570497,0.8676586361

Calculated Structures for Diels-Alder Cycloadditions

TS for Diels-Alder reaction of butadiene with isopropylaldehyde in gas phase:
b3lyp/6-31g*
E(RB3LYP) = -465.816375613

Zero-point correction= 0.235675 (Hartree/Particle)
Thermal correction to Energy= 0.248092
Thermal correction to Enthalpy= 0.249036
Thermal correction to Gibbs Free Energy= 0.197705
Sum of electronic and ZPE= -465.580700
Sum of electronic and thermal Energies= -465.568283
Sum of electronic and thermal Enthalpies= -465.567339
Sum of electronic and thermal Free Energies= -465.618670

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 155.680 46.717 108.035

C,0,-0.3525452997,-0.0059277024,0.0016694661
C,0,-0.1247277268,0.1399841802,1.3895858241

C,0,0.6129521437,-0.3799303423,-0.8894852692
C,0,1.1223458329,-0.0930399841,1.9810340048
H,0,-0.8994482919,0.6235808752,1.9788406366
H,0,-1.3055987499,0.3481301732,-0.3850013958
H,0,0.4254290174,-0.352699878,-1.9588699629
C,0,2.4142256851,1.5886519269,0.0926574571
H,0,1.5373638269,-0.8512665654,-0.5822067031
H,0,1.1872588885,-0.0180690419,3.0643523493
H,0,1.7494108792,-0.8795390041,1.5697162661
C,0,2.3366630983,1.3911727308,1.481967735
H,0,3.2135018144,1.0108409631,2.0015800513
H,0,1.7784741371,2.1478954677,2.0238668462
C,0,3.5978233363,1.1834632462,-0.7741308287
C,0,1.3728816111,2.4322729868,-0.4780543128
C,0,4.6005231304,2.3570233912,-0.8707325461
C,0,4.3267703039,-0.0863905516,-0.3083133265
H,0,3.2227968243,0.9999470679,-1.7908167828
H,0,5.4261686719,2.1080163114,-1.5492088232
H,0,4.116752437,3.2658793461,-1.2447035671
H,0,5.0258667625,2.5865323446,0.1137363861
H,0,5.1289382344,-0.3407615819,-1.01021445
H,0,4.7903752899,0.0521161545,0.6757861433
H,0,3.6572694994,-0.9509139378,-0.2443158216
O,0,0.4520374627,2.9236383855,0.1752920687
H,0,1.4467731809,2.6151820383,-1.5730184447

<u>*p*-chlorobenzaldehyde:</u>
*b3lyp/6-31+g** in gas phase*
E(RB3LYP) = -805.191743507

Zero-point correction= 0.100133 (Hartree/Particle)
Thermal correction to Energy= 0.107643
Thermal correction to Enthalpy= 0.108587
Thermal correction to Gibbs Free Energy= 0.067327
Sum of electronic and ZPE= -805.091611
Sum of electronic and thermal Energies= -805.084101
Sum of electronic and thermal Enthalpies= -805.083157
Sum of electronic and thermal Free Energies= -805.124417

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 67.547 27.788 86.840

C,0,0.0158770346,0.,-0.0950805018
C,0,-0.02870609,0.,1.3089967835
C,0,1.1484473997,0.,2.0492041626
C,0,2.3761334637,0.,1.3754882901
C,0,2.4444767416,0.,-0.0190185688

C,0,1.2560083665,0.,-0.748490227
H,0,-0.9954961604,0.,1.8024446439
H,0,1.125906585,0.,3.1333315044
Cl,0,3.862241572,0.,2.3061922491
H,0,3.4070911902,0.,-0.5178960253
H,0,1.2932066231,0.,-1.8352390019
C,0,-1.2319449786,0.,-0.8917918784
O,0,-2.3557068413,0.,-0.4215029702
H,0,-1.0827869061,0.,-1.9928964605

*b3lyp/6-31+g** with PCM solvent model*
scrf=(solvent=chloroform)
E(RB3LYP) = -805.197044258

Zero-point correction= 0.100038 (Hartree/Particle)
Thermal correction to Energy= 0.107600
Thermal correction to Enthalpy= 0.108545
Thermal correction to Gibbs Free Energy= 0.067134
Sum of electronic and ZPE= -805.097006
Sum of electronic and thermal Energies= -805.089444
Sum of electronic and thermal Enthalpies= -805.088500
Sum of electronic and thermal Free Energies= -805.129910

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 67.520 27.873 87.155

C,0,0.013584892,0.,-0.0923098116
C,0,-0.0295277725,0.,1.312642731
C,0,1.1485903741,0.,2.0515135368
C,0,2.3738056493,0.,1.3734656259
C,0,2.4427800017,0.,-0.0208363211
C,0,1.2534148658,0.,-0.7487209372
H,0,-0.9917996247,0.,1.8141421195
H,0,1.1255301038,0.,3.1354239293
Cl,0,3.8635040044,0.,2.3038421131
H,0,3.4032394614,0.,-0.5234125748
H,0,1.290547431,0.,-1.8347861128
C,0,-1.2267111618,0.,-0.8942404286
O,0,-2.358448422,0.,-0.4308196344
H,0,-1.0737618025,0.,-1.9921622353

*b3lyp-d3/6-31+g** with PCM solvent model*
b3lyp/6-31+g**
scrf=(solvent=chloroform)
EmpiricalDispersion=GD3
E(RB3LYP) = -805.207118200

Zero-point correction= 0.100099 (Hartree/Particle)
Thermal correction to Energy= 0.107645
Thermal correction to Enthalpy= 0.108589
Thermal correction to Gibbs Free Energy= 0.067214
Sum of electronic and ZPE= -805.107020
Sum of electronic and thermal Energies= -805.099473
Sum of electronic and thermal Enthalpies= -805.098529
Sum of electronic and thermal Free Energies= -805.139904

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 67.548 27.837 87.082

C,0,0.0155266669,0.,-0.0945039602
C,0,-0.0296958399,0.,1.3103288946
C,0,1.1472074738,0.,2.0508104887
C,0,2.3733010498,0.,1.373597751
C,0,2.4439080497,0.,-0.0210271285
C,0,1.2555958163,0.,-0.7505932372
H,0,-0.9937099486,0.,1.8084543619
H,0,1.1242423666,0.,3.134653983
Cl,0,3.8624307876,0.,2.3055008673
H,0,3.4056001858,0.,-0.5211069235
H,0,1.2948235601,0.,-1.8365926613
C,0,-1.2275168594,0.,-0.8924025317
O,0,-2.3565457439,0.,-0.4217981936
H,0,-1.0804195649,0.,-1.9915797106

*b3lyp/6-31+g** with SMD solvent model*
scrf=(smd, solvent=chloroform)
E(RB3LYP) = -805.205100570

Zero-point correction= 0.100208 (Hartree/Particle)
Thermal correction to Energy= 0.107721
Thermal correction to Enthalpy= 0.108665
Thermal correction to Gibbs Free Energy= 0.067394
Sum of electronic and ZPE= -805.104893
Sum of electronic and thermal Energies= -805.097379
Sum of electronic and thermal Enthalpies= -805.096435
Sum of electronic and thermal Free Energies= -805.137706

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 67.596 27.791 86.863

C,0,0.0135504404,0.,-0.0919703151
C,0,-0.0297716336,0.,1.312956565

C,0,1.1484193184,0.,2.0518760324
C,0,2.3723321003,0.,1.372352862
C,0,2.4432844815,0.,-0.0214441375
C,0,1.2533501259,0.,-0.7488478881
H,0,-0.9909443072,0.,1.8171983513
H,0,1.1237022528,0.,3.1361999417
Cl,0,3.8641995905,0.,2.3053794516
H,0,3.4034012911,0.,-0.5256970719
H,0,1.2891376082,0.,-1.8354069512
C,0,-1.2252999872,0.,-0.8951530986
O,0,-2.3576773033,0.,-0.4309520764
H,0,-1.0729359776,0.,-1.9927496651

*m062x/6-31+g** with PCM solvent model*
scrf=(solvent=chloroform)
E(RM062X) = -805.012461754

Zero-point correction= 0.100950 (Hartree/Particle)
Thermal correction to Energy= 0.108520
Thermal correction to Enthalpy= 0.109464
Thermal correction to Gibbs Free Energy= 0.067953
Sum of electronic and ZPE= -804.911512
Sum of electronic and thermal Energies= -804.903942
Sum of electronic and thermal Enthalpies= -804.902998
Sum of electronic and thermal Free Energies= -804.944509

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 68.097 27.723 87.367

C,0,0.0236465945,0.,-0.0918184882
C,0,-0.0281423855,0.,1.3066866974
C,0,1.1461948162,0.,2.0462760557
C,0,2.3681169999,0.,1.3704465332
C,0,2.4416496897,0.,-0.0193537053
C,0,1.2557804107,0.,-0.7481402903
H,0,-0.9946586329,0.,1.8009792028
H,0,1.1259736286,0.,3.1303871364
Cl,0,3.8447677588,0.,2.2979449886
H,0,3.4050541061,0.,-0.5164027965
H,0,1.2915282416,0.,-1.8344276884
C,0,-1.2236513571,0.,-0.8902499786
O,0,-2.3380123478,0.,-0.4100999816
H,0,-1.0834995227,0.,-1.9884856852

(*E*)-1-dimethylamino-3-trimethylsiloxy-1,3-butadiene:
*b3lyp/6-31+g** in gas phase*
E(RB3LYP) = -773.947747868

Zero-point correction= 0.264316 (Hartree/Particle)
Thermal correction to Energy= 0.281795
Thermal correction to Enthalpy= 0.282739
Thermal correction to Gibbs Free Energy= 0.218270
Sum of electronic and ZPE= -773.683432
Sum of electronic and thermal Energies= -773.665953
Sum of electronic and thermal Enthalpies= -773.665008
Sum of electronic and thermal Free Energies= -773.729477

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	176.829	61.937	135.687

C,0,-0.1767348345,0.3841086857,-0.3936744994
C,0,-0.2257766298,1.1750620803,0.8388738801
H,0,0.7581788586,-0.1354962508,-0.5769621423
O,0,1.0302909058,1.5906400118,1.2064984766
C,0,-1.3435079004,1.4683925618,1.5392583904
C,0,-1.2017684614,0.3231478172,-1.2784286504
N,0,-1.3000458747,-0.4857347825,-2.3916756114
H,0,-2.0785584716,0.9469226129,-1.1169875742
H,0,-1.3331439215,2.1276216879,2.3983412467
H,0,-2.2951446966,1.0374635437,1.2554133214
C,0,-2.1133623276,-0.0104677354,-3.5025962135
C,0,-0.1713532112,-1.3258652041,-2.7491145924
H,0,-2.4435621894,-0.8593001685,-4.1095043029
H,0,-2.9998208285,0.4995543698,-3.115666253
H,0,-1.5690975978,0.6927246643,-4.1547353726
H,0,-0.4734913442,-2.0165780524,-3.5407903175
H,0,0.6938240274,-0.7416391292,-3.1056157018
H,0,0.1438295749,-1.9111811353,-1.8804973642
Si,0,1.6402381926,2.2771422244,2.6282045195
C,0,3.4938977025,2.3279354569,2.3186894493
C,0,0.9743961556,4.0261312339,2.870486778
C,0,1.2364569594,1.1866865453,4.1127164117
H,0,1.6667097161,1.6111038722,5.0280575051
H,0,0.1575814596,1.0835373434,4.2637392898
H,0,1.6522028237,0.1813141844,3.9818079513
H,0,4.0255620107,2.76251353,3.1733664106
H,0,3.8897774293,1.3204479878,2.1507001306
H,0,3.7261869293,2.9307883929,1.4339648882
H,0,1.5038633374,4.5228592823,3.6928587579
H,0,1.1243918558,4.626482617,1.9660894191
H,0,-0.0942336495,4.0411057522,3.1072897692

*b3lyp/6-31+g** with PCM solvent model*
scrf=(solvent=chloroform)

E(RB3LYP) = -773.951373282

Zero-point correction= 0.263920 (Hartree/Particle)
Thermal correction to Energy= 0.281356
Thermal correction to Enthalpy= 0.282300
Thermal correction to Gibbs Free Energy= 0.217650
Sum of electronic and ZPE= -773.687453
Sum of electronic and thermal Energies= -773.670017
Sum of electronic and thermal Enthalpies= -773.669073
Sum of electronic and thermal Free Energies= -773.733723

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 176.554 61.992 136.067

C,0,-0.0385360159,0.051515605,-0.1308462247
C,0,-0.0901249449,0.1498917439,1.3288891922
H,0,0.9444115388,-0.1367696251,-0.5509424037
O,0,1.1306772682,0.4923054832,1.8871145558
C,0,-1.154621246,-0.1078703193,2.1188861676
C,0,-1.126137481,0.2049417755,-0.9323045479
N,0,-1.196221859,0.0057550074,-2.2894838814
H,0,-2.0758508724,0.495451106,-0.4874544697
H,0,-1.102253179,0.0332709918,3.1921195134
H,0,-2.0800686621,-0.4837147837,1.6986793297
C,0,-2.2191099995,0.7266782342,-3.0396071131
C,0,0.014727154,-0.3278089155,-3.0215914677
H,0,-2.462192616,0.1775524646,-3.9538392303
H,0,-3.1261296984,0.8111688665,-2.4357146568
H,0,-1.8932042971,1.7409263924,-3.3191898182
H,0,-0.2513864169,-0.6201880667,-4.0399639838
H,0,0.7185450875,0.5187856854,-3.0731448557
H,0,0.5218802519,-1.1688149927,-2.5402964616
Si,0,1.5945617427,2.0021539015,2.5083438255
C,0,3.4525709228,1.8405474282,2.7386428933
C,0,1.1598920067,3.362773958,1.279146892
C,0,0.7414604658,2.3249132384,4.1581771732
H,0,1.100252903,3.2652314876,4.5944896425
H,0,-0.344687999,2.4045549652,4.0409446069
H,0,0.9491121044,1.5214079604,4.8737895562
H,0,3.8746449653,2.7594278977,3.1621743916
H,0,3.6917081989,1.0153154525,3.4186143102
H,0,3.9518642119,1.6474620579,1.7827966337
H,0,1.468905164,4.3400828261,1.6691979166
H,0,1.6623566226,3.2071688924,0.3183440508
H,0,0.0807406789,3.403307281,1.0941364633

*B3lyp-d3/6-31+g** with PCM solvent model*

b3lyp/6-31+g**
scrf=(solvent=chloroform)
EmpiricalDispersion=GD3
E(RB3LYP) = -773.976319595

Zero-point correction= 0.264274 (Hartree/Particle)
Thermal correction to Energy= 0.281552
Thermal correction to Enthalpy= 0.282496
Thermal correction to Gibbs Free Energy= 0.219128
Sum of electronic and ZPE= -773.712046
Sum of electronic and thermal Energies= -773.694768
Sum of electronic and thermal Enthalpies= -773.693824
Sum of electronic and thermal Free Energies= -773.757191

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 176.676 61.754 133.368

C,0,0.1517072863,0.0154993942,0.0234173828
C,0,0.3342971112,-0.3461319314,1.4308784006
H,0,1.0533600078,0.2508210394,-0.5324169971
O,0,1.401320659,0.2657196155,2.0628323418
C,0,-0.4124252448,-1.2280311937,2.1269917431
C,0,-1.072661233,0.0816717815,-0.5628470932
N,0,-1.3490798622,0.2892950835,-1.892146833
H,0,-1.9579829497,-0.0610859746,0.0536933701
H,0,-0.2462040236,-1.3723535275,3.1888117367
H,0,-1.174696215,-1.8192704718,1.6338769248
C,0,-2.6288203958,0.901058797,-2.237419685
C,0,-0.2491408609,0.5653529602,-2.8031813302
H,0,-2.9079551607,0.623196513,-3.257808592
H,0,-3.4051398257,0.5407141118,-1.5575898286
H,0,-2.5929075512,1.9999573826,-2.1722691848
H,0,-0.6213400631,0.5596607143,-3.8300620077
H,0,0.2175236035,1.543693022,-2.6042751783
H,0,0.5178944663,-0.2087662666,-2.7084326011
Si,0,1.6450416209,1.942797245,2.2051263472
C,0,2.9067373261,2.094834557,3.5862682141
C,0,2.3331739502,2.6638769957,0.6062361681
C,0,0.0059959994,2.7544700924,2.6436018535
H,0,0.1255115405,3.8395517397,2.7446169888
H,0,-0.7360743525,2.5651851873,1.860126468
H,0,-0.388201736,2.3642944043,3.5883192416
H,0,3.1611670697,3.1459292939,3.7656110317
H,0,2.5172232193,1.6725696417,4.5189102279
H,0,3.8293252786,1.5618745672,3.3301727178
H,0,2.6691128514,3.6950151871,0.771061788
H,0,3.1924589577,2.0816437511,0.2544115295

H,0,1.5785645263,2.6743802884,-0.186407145

*b3lyp/6-31+g** with SMD solvent model*
scrf=(smd,solvent=chloroform)
E(RB3LYP) = -773.959329615

Zero-point correction= 0.263942 (Hartree/Particle)
Thermal correction to Energy= 0.281140
Thermal correction to Enthalpy= 0.282084
Thermal correction to Gibbs Free Energy= 0.219110
Sum of electronic and ZPE= -773.695387
Sum of electronic and thermal Energies= -773.678190
Sum of electronic and thermal Enthalpies= -773.677246
Sum of electronic and thermal Free Energies= -773.740219

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 176.418 61.880 132.540

C,0,0.0010099322,0.0305623339,-0.1174792725
C,0,-0.0253446181,0.0510764786,1.3462876529
H,0,0.9812703495,-0.0922467447,-0.5682294329
O,0,1.1766173564,0.4484635534,1.9087990028
C,0,-1.0518280425,-0.3220665211,2.1409993385
C,0,-1.1119073046,0.1770919023,-0.8867645399
N,0,-1.206239195,0.0474944214,-2.2498583938
H,0,-2.0621463594,0.4043700612,-0.4071550456
H,0,-0.987244589,-0.2276186768,3.2196729906
H,0,-1.9562892666,-0.7460100047,1.7191275043
C,0,-2.271559408,0.7717429905,-2.9350533534
C,0,-0.0015089965,-0.1898306974,-3.0287369569
H,0,-2.5271299671,0.2595393458,-3.8675526877
H,0,-3.1623441505,0.8030401094,-2.302116426
H,0,-1.9802864876,1.8068298611,-3.1748237128
H,0,-0.2824070356,-0.4332600789,-4.0565607638
H,0,0.6633261733,0.6891050039,-3.0484462495
H,0,0.5547025473,-1.0351921148,-2.6130898147
Si,0,1.5948632023,1.9948617426,2.4730195546
C,0,3.4184875117,1.8361880565,2.8900069548
C,0,1.2978657217,3.2816904394,1.1301136413
C,0,0.5854174931,2.4283197231,4.0028358128
H,0,0.8999657345,3.40223344,4.4006435277
H,0,-0.4857284392,2.4955224665,3.7796746257
H,0,0.7201662402,1.6857774995,4.7982121967
H,0,3.8108897239,2.7767497311,3.296316634
H,0,3.5851273983,1.0524836614,3.6388181864
H,0,4.009126226,1.5818536041,2.0019612175
H,0,1.5867652823,4.277912601,1.4900498785

H,0,1.8828543015,3.0699729282,0.2274955618
H,0,0.2412946656,3.3307668834,0.8419403683

*m062x/6-31+g** with PCM solvent model*
scrf=(solvent=chloroform)
E(RM062X) = -773.662510964

Zero-point correction= 0.266043 (Hartree/Particle)
Thermal correction to Energy= 0.283297
Thermal correction to Enthalpy= 0.284241
Thermal correction to Gibbs Free Energy= 0.220393
Sum of electronic and ZPE= -773.396468
Sum of electronic and thermal Energies= -773.379214
Sum of electronic and thermal Enthalpies= -773.378270
Sum of electronic and thermal Free Energies= -773.442118

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 177.771 61.512 134.380

C,0,0.0553621636,-0.0419122571,-0.0822361068
C,0,0.0269495989,-0.0147390565,1.3830314831
H,0,1.0206047379,-0.2419601111,-0.5370380677
O,0,1.2320725049,0.3481564278,1.9469763652
C,0,-1.019499507,-0.329346817,2.1644281815
C,0,-1.0435027253,0.2067429197,-0.8311205427
N,0,-1.154077766,0.0993544126,-2.1936410276
H,0,-1.9661876746,0.5084407292,-0.3362498021
H,0,-0.9521512148,-0.2267053021,3.2416533455
H,0,-1.9363660009,-0.7129103332,1.7339720373
C,0,-2.123002467,0.9549368272,-2.8597727548
C,0,0.0440117643,-0.1962262343,-2.9515095733
H,0,-2.4021798442,0.5129755471,-3.8193359669
H,0,-3.0195220463,1.0384488573,-2.2415620991
H,0,-1.7257728115,1.9647079806,-3.0401517719
H,0,-0.2260046221,-0.3616821374,-3.996136364
H,0,0.7760263429,0.6255001041,-2.9002522109
H,0,0.5133399398,-1.1040748738,-2.5633999671
Si,0,1.5441973979,1.938898859,2.4289922249
C,0,3.3684422454,1.9530110403,2.8298721322
C,0,1.1211611536,3.1059395136,1.0254657161
C,0,0.5149761185,2.3584916183,3.9383808591
H,0,0.7764871437,3.3564704785,4.3070375694
H,0,-0.5535936748,2.3561987837,3.7015603892
H,0,0.6904782968,1.640794845,4.7460499147
H,0,3.676008542,2.9366623358,3.1991301174
H,0,3.599890514,1.2126407846,3.6017896225
H,0,3.9643337594,1.7194453387,1.9424070958

H,0,1.3278953702,4.1412911411,1.3174133409
H,0,1.7072223689,2.8765181555,0.1300234016
H,0,0.0601863918,3.0313544229,0.7643304586

TS for the formation of exo-DA product for the reaction of (*E*)-1-dimethylamino-3-trimethylsiloxy-1,3-butadiene with *p*-chlorobenzaldehyde:
*b3lyp/6-31+g** in gas phase*
E(RB3LYP) = -1579.09793671

Zero-point correction= 0.366802 (Hartree/Particle)
Thermal correction to Energy= 0.391862
Thermal correction to Enthalpy= 0.392806
Thermal correction to Gibbs Free Energy= 0.309395
Sum of electronic and ZPE= -1578.731135
Sum of electronic and thermal Energies= -1578.706075
Sum of electronic and thermal Enthalpies= -1578.705131
Sum of electronic and thermal Free Energies= -1578.788542

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 245.897 91.696 175.553

C,0,0.0698476884,-0.1356232668,0.0155585702
C,0,-0.1199502056,0.0979069337,1.3767712254
H,0,0.9960551782,0.2488208313,-0.4024825203
O,0,0.970602363,0.4873064373,2.0937442749
C,0,-1.3963210631,0.2057739357,2.0005350565
C,0,-0.9244035501,-0.4414389295,-0.9309348565
H,0,-0.8451859662,0.0519803199,-1.897171972
N,0,-1.853039857,-1.4077074777,-0.9104201937
O,0,-2.2535278094,1.5124249878,-0.1526759498
H,0,-1.3654408161,0.4000445696,3.070100925
C,0,-2.2623628245,1.6952998525,1.1175239683
H,0,-2.1519623889,-0.5188856032,1.7293175028
C,0,-3.5963886732,1.6761184883,1.8477729503
H,0,-1.6142200703,2.4998926573,1.5247594767
C,0,-2.9388679114,-1.3786516956,-1.8834360158
C,0,-1.9598313032,-2.4172523187,0.130644291
H,0,-3.1465575165,-2.3930345707,-2.2386175904
H,0,-3.8460077317,-0.9615549351,-1.430546113
H,0,-2.6607756228,-0.7460617226,-2.7282331834
H,0,-2.7815626275,-2.2053525112,0.8267347093
H,0,-2.1552469201,-3.385214502,-0.3428462602
H,0,-1.0248243407,-2.468855929,0.6885471166
C,0,-3.7128617249,2.1204820034,3.171921574
C,0,-4.9439877865,2.1245208396,3.8293786314
C,0,-6.076624538,1.6792399636,3.1458446913
C,0,-5.9939829614,1.2470990003,1.8222665856

C,0,-4.753115476,1.2546811164,1.1812880787
H,0,-2.8306932634,2.4744986236,3.701007395
H,0,-5.0271720597,2.4713921236,4.8539594374
Cl,0,-7.6385978967,1.678907827,3.9649145786
H,0,-6.8887172744,0.9255027589,1.2992581396
H,0,-4.6650340014,0.9600472587,0.1404668368
Si,0,1.779558747,1.9610198232,2.3365909516
C,0,3.4931861563,1.4414021043,2.9025279397
C,0,1.83334804,2.9454240366,0.73261729
C,0,0.9025539057,2.9426943093,3.6843159316
H,0,1.477232579,3.8410567063,3.9408435124
H,0,-0.0939676347,3.2676590465,3.3664667978
H,0,0.7915187845,2.3453420011,4.5960943137
H,0,2.2692180658,3.9352012492,0.9153493221
H,0,2.4454404052,2.4496706416,-0.0289471988
H,0,0.8312160219,3.0940180839,0.3159128355
H,0,4.1139180527,2.3153657189,3.1322161684
H,0,3.4365798698,0.8226386801,3.8047959335
H,0,4.0024789581,0.8586595326,2.1274068419

*b3lyp/6-31+g** with PCM solvent model*
scrf=(solvent=chloroform)
E(RB3LYP) = -1579.11381851

Zero-point correction= 0.366840 (Hartree/Particle)
Thermal correction to Energy= 0.392063
Thermal correction to Enthalpy= 0.393007
Thermal correction to Gibbs Free Energy= 0.309114
Sum of electronic and ZPE= -1578.746978
Sum of electronic and thermal Energies= -1578.721756
Sum of electronic and thermal Enthalpies= -1578.720812
Sum of electronic and thermal Free Energies= -1578.804704

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 246.023 91.691 176.567

C,0,-0.1483649099,0.5207396029,0.0919312341
C,0,-0.5463429179,0.8257820985,1.4038881879
H,0,0.6217299792,1.1611877377,-0.3270713281
O,0,0.2398256391,1.6102840295,2.1674548362
C,0,-1.8679986387,0.6435874363,1.9201146479
C,0,-0.7680121971,-0.2873273368,-0.8664903969
H,0,-0.6333643908,0.0226406464,-1.9009311211
N,0,-1.4111117424,-1.4522658364,-0.7569114625
O,0,-2.9732743386,1.8066426641,-0.1338440312
H,0,-1.933226324,0.7750814161,2.9984566942
C,0,-2.9075363563,1.9590270256,1.1476578401

H,0,-2.4150341615,-0.2193319294,1.5641666093
C,0,-4.1955057773,1.7911169469,1.9558895366
H,0,-2.3548766076,2.8466150588,1.5287618849
C,0,-2.133091671,-1.99966954,-1.9060413525
C,0,-1.471401319,-2.2509969444,0.4604658276
H,0,-1.8579785102,-3.0485361855,-2.0506202078
H,0,-3.2137798334,-1.9359731321,-1.7375377399
H,0,-1.8865881106,-1.4317214961,-2.8037903099
H,0,-2.4533768482,-2.1815657144,0.9423173681
H,0,-1.2940409004,-3.2971384744,0.1938598902
H,0,-0.7044442605,-1.9201398029,1.1599459966
C,0,-4.3213886381,2.343238309,3.2380790692
C,0,-5.5005169865,2.2091327143,3.9748197844
C,0,-6.5679434387,1.5089214764,3.4115305306
C,0,-6.477548975,0.9553906609,2.1343563095
C,0,-5.289562971,1.1057460985,1.4140039947
H,0,-3.4879882882,2.8931006483,3.6705518363
H,0,-5.5906146163,2.6440746308,4.9646370671
Cl,0,-8.0692025643,1.3315590027,4.3308679504
H,0,-7.3225162854,0.4253063682,1.7071003933
H,0,-5.2048252004,0.7050494374,0.4087076375
Si,0,1.8909360734,2.0822721048,2.1238724576
C,0,2.9666969236,0.5504258074,1.9372989497
C,0,2.1805590616,3.323326069,0.7385899
C,0,2.1220138673,2.8903918966,3.8003232054
H,0,3.151816677,3.2472342633,3.9171120065
H,0,1.4517069107,3.7487793807,3.9173696843
H,0,1.9140887918,2.1831427193,4.610400169
H,0,3.1699191773,3.7808317794,0.8618504105
H,0,2.1492854146,2.8708627814,-0.2576587695
H,0,1.4352043836,4.1254681775,0.7708063494
H,0,4.024740219,0.8323951036,1.9969761675
H,0,2.7660436243,-0.1687412073,2.7391500868
H,0,2.8084140365,0.0465125073,0.978724206

*B3lyp-d3/6-31+g** with PCM solvent model*
b3lyp/6-31+g**
scrf=(solvent=chloroform)
EmpiricalDispersion=GD3
E(RB3LYP) = -1579.16046946

Zero-point correction= 0.367496 (Hartree/Particle)
Thermal correction to Energy= 0.392236
Thermal correction to Enthalpy= 0.393180
Thermal correction to Gibbs Free Energy= 0.311998

Sum of electronic and ZPE= -1578.792973
Sum of electronic and thermal Energies= -1578.768233
Sum of electronic and thermal Enthalpies= -1578.767289
Sum of electronic and thermal Free Energies= -1578.848472

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	246.132	91.349	170.864

C,0,0.1114473181,-0.2652971423,0.0509011311
C,0,-0.0416231552,0.0092822524,1.4063235937
H,0,1.0689192034,0.0190441033,-0.3760358847
O,0,1.0955751353,0.337305694,2.0856613344
C,0,-1.2952775732,0.2394769995,2.0476556225
C,0,-0.9099467342,-0.4997378059,-0.889310812
H,0,-0.7801011951,-0.0414924045,-1.8666042328
N,0,-1.9588711519,-1.3182219088,-0.82168957
O,0,-1.8900733438,1.7895673104,-0.0532574784
H,0,-1.2331071505,0.4294993081,3.1170124066
C,0,-2.0226994136,1.8204289971,1.2275010807
H,0,-2.1085948624,-0.4238688755,1.7914587278
C,0,-3.4200369892,1.7517651358,1.8171719386
H,0,-1.4088855298,2.5569399975,1.7838031305
C,0,-3.0150340493,-1.2435778761,-1.8293072897
C,0,-2.1792869662,-2.2916830797,0.239709084
H,0,-3.2236705235,-2.2418436628,-2.226044116
H,0,-3.929670764,-0.8437331359,-1.3780224403
H,0,-2.7113705754,-0.5819207437,-2.6409753017
H,0,-2.9899067971,-1.9778548653,0.9078328692
H,0,-2.4633507941,-3.2436054311,-0.2188055295
H,0,-1.2651009995,-2.4262655439,0.8168571504
C,0,-3.6649633616,2.1020552548,3.151780506
C,0,-4.9500490029,2.0304359285,3.6933522444
C,0,-6.000323641,1.6016365798,2.8795605785
C,0,-5.7886946181,1.2566865917,1.5439659133
C,0,-4.4959051112,1.33932929,1.0221690864
H,0,-2.8428548603,2.4363892427,3.7804269651
H,0,-5.1353056561,2.3049878501,4.7263373662
Cl,0,-7.632917938,1.5042890752,3.5526445866
H,0,-6.620730254,0.9399188894,0.9238131556
H,0,-4.3023656632,1.1010970534,-0.0185427536
Si,0,1.7433805551,1.8950254984,2.3658452832
C,0,3.5529304997,1.5741519379,2.73556595
C,0,1.4821273139,2.9164932494,0.8118071075
C,0,0.8882522903,2.654974512,3.8595533954
H,0,1.3583783139,3.6104765784,4.1215139474
H,0,-0.1724594979,2.8450375307,3.668295513
H,0,0.9657025756,1.9904192355,4.7274352041

H,0,1.6672331894,3.9780164553,1.0132747851
H,0,2.1664206177,2.5986264196,0.0169519782
H,0,0.4589151884,2.8068554605,0.4336434728
H,0,4.0718958622,2.514115969,2.9567714131
H,0,3.6643113597,0.9140907546,3.6029452179
H,0,4.0492117496,1.1031423205,1.8801956698

*b3lyp/6-31+g** with SMD solvent model*
scrf=(smd,solvent=chloroform)
E(RB3LYP) = -1579.13043297

Zero-point correction= 0.366914 (Hartree/Particle)
Thermal correction to Energy= 0.391935
Thermal correction to Enthalpy= 0.392879
Thermal correction to Gibbs Free Energy= 0.309534
Sum of electronic and ZPE= -1578.763519
Sum of electronic and thermal Energies= -1578.738498
Sum of electronic and thermal Enthalpies= -1578.737554
Sum of electronic and thermal Free Energies= -1578.820899

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 245.943 91.518 175.416

C,0,-0.2002845004,0.626377113,-0.0512509076
C,0,-0.6156919332,0.8968697797,1.2656832338
H,0,0.5324566918,1.3148459491,-0.4630972352
O,0,0.1482007757,1.6870559022,2.044662981
C,0,-1.9313441717,0.6728197934,1.7813133642
C,0,-0.7279122963,-0.2498538184,-1.0045143717
H,0,-0.5770815644,0.0379450127,-2.0435441336
N,0,-1.3083908777,-1.4447765812,-0.877070476
O,0,-3.0866322994,2.1010960355,-0.062407116
H,0,-1.9775264311,0.6780066813,2.8692126527
C,0,-2.9577492458,2.0890648606,1.2239476021
H,0,-2.4908935955,-0.1386527349,1.3326362359
C,0,-4.2226685859,1.8674493691,2.05846548
H,0,-2.3620213202,2.908057418,1.6850556215
C,0,-1.9261044844,-2.0879116011,-2.0368245591
C,0,-1.3751937024,-2.2055511049,0.3642661367
H,0,-1.5256978168,-3.0996167897,-2.1587191888
H,0,-3.0110587368,-2.1535884465,-1.8959841726
H,0,-1.7258185328,-1.5054950555,-2.9368969672
H,0,-2.3694184474,-2.1494910546,0.8220095708
H,0,-1.1616771905,-3.2537383025,0.1339706816
H,0,-0.6341422866,-1.834326248,1.0723393627
C,0,-4.2951885849,2.2900489883,3.3931901887
C,0,-5.4556334855,2.1109297035,4.1502262735

C,0,-6.5564273333,1.4954850302,3.5536821017
C,0,-6.5200565874,1.0703456794,2.2256764781
C,0,-5.3506311275,1.2664508879,1.4862052382
H,0,-3.4354115607,2.7746764505,3.8514807759
H,0,-5.5043642291,2.4484698198,5.1804321085
Cl,0,-8.0349939039,1.2599931759,4.501037781
H,0,-7.3905936228,0.6050211605,1.7742492199
H,0,-5.3072235098,0.9673018784,0.4431050539
Si,0,1.8267348569,2.0483248,2.1288538536
C,0,2.7830649362,0.4317177104,2.1878672233
C,0,2.3578828426,3.1227536573,0.6799289132
C,0,1.9451569881,2.9912833048,3.7442259811
H,0,2.9857895672,3.2605341109,3.9631436843
H,0,1.36047657,3.9179478166,3.7067796288
H,0,1.5699593566,2.3899576067,4.5805677424
H,0,3.3128220408,3.6103515488,0.9156802921
H,0,2.5025949769,2.5503478746,-0.2428955978
H,0,1.6251799428,3.9135053511,0.4794648161
H,0,3.8511307372,0.6321659477,2.3419559899
H,0,2.441984466,-0.2020770994,3.0150259017
H,0,2.6859202153,-0.1396625812,1.2580045571

*m062x/6-31+g** with PCM solvent model*
scrf=(solvent=chloroform)
E(RM062X) = -1578.65008332

Zero-point correction= 0.369756 (Hartree/Particle)
Thermal correction to Energy= 0.394526
Thermal correction to Enthalpy= 0.395470
Thermal correction to Gibbs Free Energy= 0.313500
Sum of electronic and ZPE= -1578.280328
Sum of electronic and thermal Energies= -1578.255558
Sum of electronic and thermal Enthalpies= -1578.254613
Sum of electronic and thermal Free Energies= -1578.336583

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 247.569 91.168 172.520

C,0,0.1104195966,-0.2949952621,0.041332185
C,0,-0.024267543,-0.0150241716,1.3979511576
H,0,1.0634023714,-0.0205445262,-0.4006934579
O,0,1.1284813585,0.2933801884,2.0537386731
C,0,-1.25240933,0.2265349375,2.056952319
C,0,-0.9354840033,-0.5066717167,-0.8711394569
H,0,-0.8205365756,-0.0615333216,-1.8575945058
N,0,-2.0087112652,-1.2758741171,-0.7587197651
O,0,-1.8241421595,1.7921072762,-0.0679863933

H,0,-1.1813392295,0.4240758436,3.125139851
C,0,-1.9628845627,1.8515778999,1.1932272079
H,0,-2.1013245459,-0.3836980591,1.7860477488
C,0,-3.3543592449,1.7663036178,1.7828621616
H,0,-1.3347024721,2.568915695,1.7583966866
C,0,-3.0666669772,-1.2148558993,-1.7575860447
C,0,-2.2214923656,-2.2467754777,0.3002246223
H,0,-3.9953615491,-0.8747498249,-1.2883682892
H,0,-2.7927723342,-0.5118208631,-2.5436166533
H,0,-3.2312325978,-2.2077790787,-2.1860502386
H,0,-3.0444889589,-1.9414441274,0.9565213862
H,0,-2.4871034458,-3.2014498042,-0.1629852662
H,0,-1.3093009849,-2.3636957027,0.884068325
C,0,-3.597900039,2.082256674,3.1214699894
C,0,-4.8814091211,1.9982495355,3.6548389305
C,0,-5.9265027788,1.5932680135,2.8284029407
C,0,-5.7134997211,1.2844579377,1.4885226209
C,0,-4.4221506816,1.3783515016,0.9729957516
H,0,-2.7752539865,2.4001368912,3.7589764824
H,0,-5.0730976296,2.2448624646,4.6938770486
Cl,0,-7.5447973239,1.481769994,3.487899816
H,0,-6.5468996154,0.9859611302,0.8608470203
H,0,-4.2218095443,1.1715850155,-0.0740750385
Si,0,1.7029582637,1.8652247877,2.3561525537
C,0,3.5143788635,1.6146735248,2.7311439012
C,0,1.4203293208,2.892100642,0.8178520191
C,0,0.8343316701,2.5778262607,3.8575039275
H,0,1.3204816731,3.5131271712,4.1563962181
H,0,-0.2204694488,2.7962450173,3.668145725
H,0,0.8960563238,1.8810004684,4.6997929385
H,0,1.5316290041,3.9578955905,1.0442786977
H,0,2.1517172418,2.6325872153,0.0449087377
H,0,0.4195169408,2.7268263455,0.4000225743
H,0,3.9979356392,2.5712350945,2.954284726
H,0,3.644225121,0.958685819,3.5975710797
H,0,4.0280226468,1.1621493994,1.8776020862

Exo-DA product for the reaction of (*E*)-1-dimethylamino-3-trimethylsiloxy-1,3-butadiene with *p*-chlorobenzaldehyde:
*b3lyp/6-31+g** in gas phase*
E(RB3LYP) = -1579.14808079

Zero-point correction= 0.371369 (Hartree/Particle)
Thermal correction to Energy= 0.395495
Thermal correction to Enthalpy= 0.396440
Thermal correction to Gibbs Free Energy= 0.315364
Sum of electronic and ZPE= -1578.776712
Sum of electronic and thermal Energies= -1578.752585

Sum of electronic and thermal Enthalpies= -1578.751641
Sum of electronic and thermal Free Energies= -1578.832717

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	248.177	89.511	170.638

C,0,-0.445322,1.104099,0.320515
C,0,-0.414687,1.020916,1.659514
H,0,0.421519,1.37662,-0.270628
O,0,0.651175,1.24249,2.47015
C,0,-1.690577,0.699925,2.387335
C,0,-1.730912,0.797893,-0.40708
H,0,-1.755176,1.378655,-1.349316
N,0,-1.883016,-0.639264,-0.716694
O,0,-2.908877,1.212674,0.294834
H,0,-1.613072,1.01808,3.430979
C,0,-2.853917,1.446189,1.707645
H,0,-1.87988,-0.37974,2.376352
C,0,-4.19936,1.078581,2.302529
H,0,-2.688117,2.522747,1.863588
C,0,-3.064785,-0.871013,-1.551111
C,0,-0.698249,-1.211596,-1.353378
H,0,-3.214392,-1.948168,-1.674359
H,0,-3.94705,-0.445068,-1.0729
H,0,-2.96402,-0.419977,-2.558031
H,0,-0.883339,-2.270396,-1.557608
H,0,-0.445348,-0.723494,-2.31619
H,0,0.165121,-1.138956,-0.689405
C,0,-4.889668,1.985846,3.112616
C,0,-6.111426,1.647256,3.701786
C,0,-6.645642,0.382439,3.466242
C,0,-5.981722,-0.540886,2.655743
C,0,-4.762081,-0.186249,2.080168
H,0,-4.47592,2.97609,3.286171
H,0,-6.642372,2.356989,4.326746
Cl,0,-8.186964,-0.057928,4.195788
H,0,-6.414905,-1.51943,2.478673
H,0,-4.244497,-0.894972,1.441102
Si,0,2.284317,1.600607,2.147323
C,0,3.044056,1.68049,3.861898
C,0,3.060569,0.219083,1.127611
C,0,2.419111,3.261174,1.266998
H,0,3.471877,3.550909,1.163849
H,0,1.981286,3.240867,0.263846
H,0,1.91166,4.047343,1.83704
H,0,4.139873,0.38559,1.026254
H,0,2.917856,-0.752562,1.613459

H,0,2.640304,0.155397,0.118867
H,0,4.114654,1.91027,3.809283
H,0,2.562226,2.45492,4.468413
H,0,2.929158,0.725149,4.385256

*b3lyp/6-31+g** with PCM solvent model*
scrf=(solvent=chloroform)
E(RB3LYP) = -1579.15708344

Zero-point correction= 0.370893 (Hartree/Particle)
Thermal correction to Energy= 0.395132
Thermal correction to Enthalpy= 0.396076
Thermal correction to Gibbs Free Energy= 0.313919
Sum of electronic and ZPE= -1578.786190
Sum of electronic and thermal Energies= -1578.761952
Sum of electronic and thermal Enthalpies= -1578.761007
Sum of electronic and thermal Free Energies= -1578.843164

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 247.949 89.647 172.914

C,0,-0.5089389296,1.0164103049,0.4359513172
C,0,-0.5120057525,1.2446412211,1.7592996752
H,0,0.3916873062,1.1679975231,-0.144728389
O,0,0.5724840154,1.5977748792,2.5039057355
C,0,-1.7727255913,1.1709500384,2.5784821253
C,0,-1.7708298008,0.6358045264,-0.3065376779
H,0,-2.1233543369,1.5124231834,-0.9011125182
N,0,-1.6046709223,-0.5145852998,-1.1995214246
O,0,-2.8225588545,0.2833059175,0.5930666323
H,0,-1.7910680761,2.0107854894,3.2826771195
C,0,-3.0015186694,1.2207863237,1.6565290998
H,0,-1.7842575585,0.2501716109,3.1759798266
C,0,-4.2902579134,0.8943928778,2.3805832518
H,0,-3.0812943207,2.2342545325,1.2331298939
C,0,-2.8509634299,-0.7962737426,-1.9230363436
C,0,-0.5065716245,-0.3395808634,-2.152557233
H,0,-2.7089810904,-1.687264394,-2.5407382593
H,0,-3.659455658,-0.9860622814,-1.2176574986
H,0,-3.1501925631,0.0401117364,-2.5837828062
H,0,-0.4893682557,-1.2019889457,-2.8238152918
H,0,-0.614543027,0.5706238426,-2.7735825576
H,0,0.4567920557,-0.3021557605,-1.6415560528
C,0,-5.0764923286,1.9238471307,2.9122233605
C,0,-6.2445948231,1.6453735602,3.6269552674
C,0,-6.6268456123,0.3161785304,3.7998180267
C,0,-5.8670312684,-0.7297871652,3.2753889267

C,0,-4.6988099429,-0.4327841012,2.5705048849
H,0,-4.7828159139,2.9603075031,2.7670383577
H,0,-6.8488380339,2.4489123609,4.0334350559
Cl,0,-8.1046523466,-0.0502105931,4.6931828528
H,0,-6.1811619405,-1.7585584118,3.4141788084
H,0,-4.1059891265,-1.2405102305,2.1544722391
Si,0,2.2520276566,1.4473446312,2.2349908122
C,0,2.9844331674,2.0152712281,3.867650762
C,0,2.6668486855,-0.3522234451,1.8740382539
C,0,2.8116438521,2.5799629607,0.8357574753
H,0,3.9067550323,2.6424359327,0.8305824282
H,0,2.4980508666,2.2255235863,-0.1513955905
H,0,2.4211038123,3.5946376022,0.9726788616
H,0,3.7479436283,-0.4684178238,1.7319096777
H,0,2.3659112962,-0.9961024719,2.7077991044
H,0,2.1688402434,-0.7164264368,0.9697543411
H,0,4.0789748852,1.9623068534,3.8409932127
H,0,2.7022009542,3.0515859952,4.0839694642
H,0,2.6345622539,1.388403084,4.6949717925

*B3lyp-d3/6-31+g** with PCM solvent model*
b3lyp/6-31+g**
EmpiricalDispersion=GD3
scrf=(solvent=chloroform)
E(RB3LYP) = -1579.19937707

Zero-point correction= 0.371828 (Hartree/Particle)
Thermal correction to Energy= 0.395588
Thermal correction to Enthalpy= 0.396532
Thermal correction to Gibbs Free Energy= 0.316920
Sum of electronic and ZPE= -1578.827549
Sum of electronic and thermal Energies= -1578.803789
Sum of electronic and thermal Enthalpies= -1578.802845
Sum of electronic and thermal Free Energies= -1578.882457

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 248.235 89.177 167.558

C,0,-0.1293888007,0.2185641591,0.05365849
C,0,-0.0575885083,0.3303861702,1.3847365282
H,0,0.754256382,0.1236449825,-0.5671667633
O,0,1.1106496885,0.3103392707,2.0960803923
C,0,-1.3376803057,0.4595080404,2.1648090207
C,0,-1.4945195981,0.2143428453,-0.5866232089
H,0,-1.4064239968,0.5520881887,-1.6347045556
N,0,-2.146480599,-1.1081694959,-0.5414775356
O,0,-2.3764976509,1.1779966128,0.0038003245

H,0,-1.1429545488,0.8666905016,3.160568994
C,0,-2.3135365323,1.4024527638,1.4264128616
H,0,-1.7954797053,-0.5272357404,2.2914593622
C,0,-3.7126739056,1.3211700298,2.0012580184
H,0,-1.9411276421,2.42742456,1.5549988465
C,0,-3.3707007457,-1.1083638131,-1.3480919739
C,0,-1.2593616366,-2.194455948,-0.9635284799
H,0,-3.9000937088,-2.055589212,-1.2065909241
H,0,-4.0232841053,-0.2934975681,-1.0323046907
H,0,-3.1596659993,-0.9872289632,-2.4278423319
H,0,-1.8041035083,-3.1412450465,-0.9029330098
H,0,-0.9025801597,-2.0753005075,-2.0046844818
H,0,-0.3916597781,-2.254638725,-0.3041314927
C,0,-4.2688797342,2.4050700522,2.6873026986
C,0,-5.5509323294,2.3273897603,3.241906895
C,0,-6.2752085112,1.1465148635,3.0945221711
C,0,-5.7458469953,0.0486562169,2.4110632298
C,0,-4.4645270712,0.1444217096,1.870035078
H,0,-3.7022251361,3.3264701133,2.7929767156
H,0,-5.978819154,3.1711160044,3.7720589312
Cl,0,-7.8981101363,1.0344420477,3.7820448863
H,0,-6.3264900689,-0.8613783729,2.3060582682
H,0,-4.0392689661,-0.6984029082,1.3340341306
Si,0,2.1166948974,1.6716128687,2.3140483282
C,0,3.4354044304,1.0763885665,3.503641426
C,0,2.8338150817,2.1762086166,0.6523839789
C,0,1.0765551458,3.0647588623,3.0334302419
H,0,1.6884618107,3.9597307326,3.1954612042
H,0,0.2625973282,3.3384652791,2.3524013462
H,0,0.6373630588,2.7756019523,3.9945146544
H,0,3.4929213023,3.0449764486,0.7659798162
H,0,3.418088929,1.3605551396,0.2122540579
H,0,2.0378099953,2.4451672826,-0.0502156461
H,0,4.1547823274,1.8761293944,3.7135626706
H,0,2.9915147894,0.7589348267,4.4533914397
H,0,3.9846663712,0.2278804378,3.0813170871

*b3lyp/6-31+g** with SMD solvent model*
scrf=(smd,solvent=chloroform)
E(RB3LYP) = -1579.17145357

Zero-point correction= 0.371121 (Hartree/Particle)
Thermal correction to Energy= 0.395048
Thermal correction to Enthalpy= 0.395992
Thermal correction to Gibbs Free Energy= 0.316137
Sum of electronic and ZPE= -1578.800333
Sum of electronic and thermal Energies= -1578.776406

Sum of electronic and thermal Enthalpies= -1578.775461
Sum of electronic and thermal Free Energies= -1578.855316

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 247.896 89.402 168.069

C,0,-0.3341428745,0.0159338722,0.4204815746
C,0,-0.2949279893,0.3987382504,1.7047436669
H,0,0.5875556173,-0.2152555882,-0.0994015727
O,0,0.8601656628,0.4179272274,2.4431783658
C,0,-1.5330428282,0.782549122,2.4702186182
C,0,-1.6376996017,-0.0646901107,-0.3426615498
H,0,-1.7191060729,0.8093658138,-1.0306625462
N,0,-1.7847704481,-1.3009683016,-1.118103216
O,0,-2.759805897,-0.017788876,0.5410315558
H,0,-1.3333020161,1.6816555837,3.0653587019
C,0,-2.6925379293,1.0477278954,1.4963703093
H,0,-1.7970425107,-0.0157582558,3.1762416966
C,0,-4.0368221811,1.1532543802,2.1845014574
H,0,-2.495235709,1.9913727284,0.9654703178
C,0,-3.0551074598,-1.3022123642,-1.8548735175
C,0,-0.674916744,-1.5136444518,-2.0510186746
H,0,-3.1536365649,-2.2509583739,-2.3899611885
H,0,-3.8938006998,-1.206229458,-1.165066227
H,0,-3.1140141451,-0.4798906781,-2.593995555
H,0,-0.895081056,-2.3969832304,-2.6564650899
H,0,-0.5215507768,-0.6613046555,-2.7404359131
H,0,0.259512085,-1.7065368793,-1.5209068498
C,0,-4.6527657586,2.3996460328,2.3465559763
C,0,-5.8777676384,2.5210378176,3.0096431227
C,0,-6.48807885,1.3713065651,3.5058718161
C,0,-5.9027539953,0.1134205311,3.353461393
C,0,-4.6762300763,0.0137261013,2.6950970907
H,0,-4.1780180205,3.2926702754,1.9483235371
H,0,-6.3473727282,3.4916713589,3.1284211907
Cl,0,-8.0398139973,1.5071731037,4.3420600458
H,0,-6.3934131259,-0.7729915583,3.7414351672
H,0,-4.2201707024,-0.9636486353,2.5708232699
Si,0,2.132823351,1.5500120982,2.4130808968
C,0,3.2088365016,1.035944784,3.8599602085
C,0,3.0744652733,1.4433991774,0.7868745975
C,0,1.4295141511,3.2820901946,2.6381634882
H,0,2.2376557076,4.0247859281,2.6220060746
H,0,0.7321495906,3.5449036118,1.8336228859
H,0,0.903647337,3.3875654228,3.5942862668
H,0,3.9482760373,2.1075028339,0.8167495164
H,0,3.4377120179,0.4263409826,0.598086229

H,0,2.4604869469,1.7507788317,-0.0676468896
H,0,4.0869950661,1.6879449648,3.9455052991
H,0,2.6555979686,1.0915597132,4.8048586614
H,0,3.567004083,0.0064462147,3.7405927918

*m062x/6-31+g** with PCM solvent model*
scrf=(solvent=chloroform)
E(RM062X) = -1578.70704558

Zero-point correction= 0.375288 (Hartree/Particle)
Thermal correction to Energy= 0.398768
Thermal correction to Enthalpy= 0.399712
Thermal correction to Gibbs Free Energy= 0.321250
Sum of electronic and ZPE= -1578.331758
Sum of electronic and thermal Energies= -1578.308277
Sum of electronic and thermal Enthalpies= -1578.307333
Sum of electronic and thermal Free Energies= -1578.385796

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 250.231 88.356 165.138

C,0,-0.1378423102,0.2708280384,0.1146154713
C,0,-0.0803107505,0.325033937,1.4466719383
H,0,0.7518365641,0.1960069185,-0.5020975287
O,0,1.0724619461,0.2893965977,2.1724464062
C,0,-1.36648409,0.41999795,2.2158819716
C,0,-1.4998947075,0.2800437898,-0.5297444456
H,0,-1.4109532407,0.6492783844,-1.5675938401
N,0,-2.1269816995,-1.0469603641,-0.5349481943
O,0,-2.3904923635,1.1972186272,0.0878297267
H,0,-1.1811322702,0.7930669584,3.2275567134
C,0,-2.327096503,1.3858498019,1.5019708832
H,0,-1.8261249362,-0.5713491183,2.2995455631
C,0,-3.7250579833,1.2891016668,2.0702265367
H,0,-1.9554448685,2.4067971061,1.6660431649
C,0,-3.3512214912,-1.0154614746,-1.3314241142
C,0,-1.2289199036,-2.0696688107,-1.0608034611
H,0,-3.8648141722,-1.977008513,-1.2448407053
H,0,-4.0121202668,-0.2271812025,-0.9680425337
H,0,-3.1388823084,-0.8289521682,-2.4001678815
H,0,-1.7597177386,-3.0245247643,-1.0884515557
H,0,-0.8893043857,-1.8392272245,-2.0880888931
H,0,-0.3536983817,-2.1780906032,-0.4184591763
C,0,-4.2762873741,2.3426502527,2.796569884
C,0,-5.5569950659,2.2443970623,3.342502164
C,0,-6.2798647414,1.0751460001,3.1446313622
C,0,-5.7530697508,0.0070566184,2.4203954151

C,0,-4.4733029525,0.121606661,1.8882180871
H,0,-3.7060430839,3.2570173672,2.9385841413
H,0,-5.986855011,3.0651712375,3.9062878776
Cl,0,-7.8893378051,0.9378629017,3.8178095177
H,0,-6.3376228166,-0.8959881069,2.2809573856
H,0,-4.0429679362,-0.7001773596,1.3195530856
Si,0,2.1085173209,1.6329960272,2.2731656302
C,0,3.3200186402,1.1795162477,3.6164948151
C,0,2.9668672837,1.9013199393,0.6308138614
C,0,1.065153295,3.1252088364,2.7152346867
H,0,1.6897082614,4.0203854927,2.8017223201
H,0,0.3179922226,3.3157758597,1.9370001247
H,0,0.5455731928,2.9791074634,3.6676585664
H,0,3.7322717407,2.6783501902,0.7327194159
H,0,3.4579205726,0.9840892939,0.2906527454
H,0,2.2619926233,2.2241523318,-0.1415654997
H,0,4.0371401897,1.9906708627,3.777733096
H,0,2.8003462219,0.9897135985,4.5602625013
H,0,3.8805128338,0.2793686893,3.3463497706

TS for the formation of endo-DA product for the reaction of (*E*)-1-dimethylamino-3-trimethylsiloxy-1,3-butadiene with *p*-chlorobenzaldehyde:
*b3lyp/6-31+g** with PCM solvent model*
scrf=(solvent=chloroform)
E(RB3LYP) = -1579.13034406

Zero-point correction= 0.366413 (Hartree/Particle)
Thermal correction to Energy= 0.391905
Thermal correction to Enthalpy= 0.392849
Thermal correction to Gibbs Free Energy= 0.308516
Sum of electronic and ZPE= -1578.763931
Sum of electronic and thermal Energies= -1578.738439
Sum of electronic and thermal Enthalpies= -1578.737495
Sum of electronic and thermal Free Energies= -1578.821828

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	245.924	92.091	177.493

C,0,-0.4413229242,0.1604661145,-0.7552751067
C,0,-0.3503269745,-0.1582879517,0.6120672877
H,0,0.4747234257,0.4821605356,-1.2373358566
O,0,0.8690894383,0.0560485346,1.1541109956
C,0,-1.4525774974,-0.5080611596,1.4462393175
C,0,-1.6442850632,0.1362438378,-1.4542979815
N,0,-1.8079225554,0.5157688515,-2.7248315202
H,0,-2.5458917087,-0.1981201978,-0.9572555765
O,0,-3.1354237508,1.3449998302,0.5848009461

H,0,-1.187410518,-0.8471221076,2.444129088
C,0,-2.5862813593,1.0192294194,1.7004398779
H,0,-2.2147015428,-1.1287177609,0.983189703
H,0,-3.2063585018,0.4652469081,2.435550632
C,0,-1.724256826,2.0464270357,2.4117255666
C,0,-1.157986659,3.112766361,1.7009668719
C,0,-0.3858876817,4.0808814883,2.3468412631
C,0,-0.1918046848,3.9815588976,3.7249081446
C,0,-0.7558397366,2.9412379138,4.4637400994
C,0,-1.5185674719,1.9800850219,3.7960389827
H,0,-1.3440209652,3.1833680837,0.6343084543
H,0,0.0512847892,4.9039351556,1.7911861822
Cl,0,0.7747095845,5.2081372545,4.5556057202
H,0,-0.6081630806,2.8872106516,5.5371945659
H,0,-1.9661527661,1.1703917704,4.3684121363
C,0,-3.1132779901,0.4277876269,-3.3766285
C,0,-0.7020897798,1.0679627358,-3.5054800949
H,0,-3.0598657245,-0.2297508891,-4.251317015
H,0,-3.8460676616,0.0282255133,-2.6753724393
H,0,-3.4423078323,1.4205163413,-3.7015512916
H,0,-1.0740872391,1.3670421804,-4.4853110381
H,0,-0.2779379489,1.9458145697,-3.0067235753
H,0,0.0894314496,0.3230109478,-3.6439376197
Si,0,1.8426699851,-0.8680003382,2.222095878
C,0,3.53880664,-0.0974551051,2.0013972948
C,0,1.2705714611,-0.7051413322,4.0065292595
C,0,1.7932074981,-2.6597850984,1.6506389532
H,0,2.4476627098,-3.274032158,2.2803602908
H,0,0.7821453629,-3.0763673186,1.7151941279
H,0,2.1359351845,-2.7550483296,0.6145024776
H,0,2.0302579315,-1.1369224536,4.66980222
H,0,1.1378541571,0.3453701664,4.284355
H,0,0.328838137,-1.2301509119,4.1964723175
H,0,4.2760023155,-0.5965710818,2.6408171437
H,0,3.8774263606,-0.1797464212,0.9630651422
H,0,3.5225720141,0.9642858678,2.2707626756

*B3lyp-d3/6-31+g** with PCM solvent model*
b3lyp/6-31+g**
EmpiricalDispersion=GD3
Scrf=(solvent=chloroform)
E(RB3LYP) = -1579.17967485

Zero-point correction= 0.367207 (Hartree/Particle)
Thermal correction to Energy= 0.392357
Thermal correction to Enthalpy= 0.393301
Thermal correction to Gibbs Free Energy= 0.310711
Sum of electronic and ZPE= -1578.812467

Sum of electronic and thermal Energies= -1578.787318
Sum of electronic and thermal Enthalpies= -1578.786374
Sum of electronic and thermal Free Energies= -1578.868963

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	246.208	91.732	173.825

C,0,-0.670915672,0.0820663802,-0.7723746948
C,0,-0.5852395432,-0.242902577,0.5925913177
H,0,0.2608944422,0.3300476364,-1.2669432206
O,0,0.6453101575,-0.1097873726,1.1153850385
C,0,-1.7084426235,-0.4594540638,1.4458165095
C,0,-1.8872872061,0.1969757229,-1.4370350285
N,0,-2.0438193563,0.6200856307,-2.6939192897
H,0,-2.8056164323,-0.0582946015,-0.9253093731
O,0,-3.0661231467,1.6476587964,0.6144167175
H,0,-1.4739096217,-0.8285336426,2.4383614644
C,0,-2.5377894186,1.2269234106,1.7112415766
H,0,-2.5540907077,-0.9721536826,0.9961280718
H,0,-3.221005981,0.823710373,2.4885977005
C,0,-1.4326740218,2.0471990807,2.3494630395
C,0,-0.6668140857,2.9206131622,1.5677853321
C,0,0.3844162464,3.6506513234,2.1250756458
C,0,0.6600605577,3.5058951747,3.485374894
C,0,-0.0970321538,2.6573169136,4.2942096421
C,0,-1.1408909724,1.9331497303,3.7141595318
H,0,-0.9073278969,3.0127011482,0.5139108955
H,0,0.9837344046,4.3188379186,1.5156977756
Cl,0,1.9975278948,4.4158087527,4.2008862632
H,0,0.1263036899,2.5654761234,5.3517978208
H,0,-1.7340812606,1.2663417411,4.3363354245
C,0,-3.3720727303,0.7366011933,-3.2921985087
C,0,-0.9067358175,1.08633028,-3.4854825302
H,0,-3.4258346653,0.1467042183,-4.2133877224
H,0,-4.124408034,0.3729504279,-2.5917399131
H,0,-3.5901236338,1.7837739909,-3.5288116349
H,0,-1.2604686858,1.3980482665,-4.4681506545
H,0,-0.4199765298,1.9381323045,-2.9973401154
H,0,-0.1711862012,0.2855044199,-3.6162848598
Si,0,1.6305949761,-0.8595330212,2.2890104291
C,0,2.9160681501,0.4539357426,2.645043093
C,0,0.7037760016,-1.3377956846,3.852200943
C,0,2.3536134796,-2.3858786945,1.4666272217
H,0,3.0414470746,-2.9021306033,2.1466178406
H,0,1.5610039986,-3.0905436398,1.1898784422
H,0,2.9060487475,-2.118901977,0.559247928
H,0,1.4328519992,-1.6929627856,4.5912012346

H,0,0.1769585325,-0.4822053609,4.2844569924
H,0,-0.0145267365,-2.1460366666,3.6810167832
H,0,3.6526797076,0.0911827212,3.3710072527
H,0,3.4475310418,0.7395591649,1.7310120481
H,0,2.4399410326,1.3498346246,3.0565596755

*B3lyp-d3/6-31+g** with PCM solvent model and an explicit $CHCl_3$ molecule*
b3lyp/6-31+g**
EmpiricalDispersion=GD3
Scrf=(solvent=chloroform)
E(RB3LYP) = -2998.48969094

Zero-point correction= 0.387713 (Hartree/Particle)
Thermal correction to Energy= 0.419465
Thermal correction to Enthalpy= 0.420409
Thermal correction to Gibbs Free Energy= 0.319816
Sum of electronic and ZPE= -2998.101977
Sum of electronic and thermal Energies= -2998.070226
Sum of electronic and thermal Enthalpies= -2998.069282
Sum of electronic and thermal Free Energies= -2998.169875

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	263.218	111.531	211.716

C,0,-0.7602066174,0.2518814715,-0.9051649847
C,0,-0.4723838642,-0.1855690077,0.4043135461
H,0,0.0410007865,0.7645118836,-1.4243780641
O,0,0.7479077064,0.1800715625,0.842909424
C,0,-1.405269604,-0.7959349875,1.2818111367
C,0,-2.0097408618,0.1042521766,-1.491861314
N,0,-2.3661571406,0.5633070964,-2.69507509
H,0,-2.7927842466,-0.4189747384,-0.9592627382
O,0,-3.2582517113,1.0994664756,0.7870686344
H,0,-1.0119611481,-1.188633519,2.214084458
C,0,-2.68555624,0.6199064424,1.8313970342
H,0,-2.1489254579,-1.4398967354,0.8232718854
H,0,-3.2591826518,-0.1038294604,2.4405929053
C,0,-1.8503395374,1.5277109359,2.7015809903
C,0,-1.021291821,2.5068326151,2.1382954726
C,0,-0.2801143231,3.3714711629,2.9415292726
C,0,-0.3812984748,3.2571285669,4.3298765739
C,0,-1.2005543338,2.295987091,4.9208013811
C,0,-1.926119269,1.4321752409,4.0962166684
H,0,-0.9424406281,2.5819622995,1.0606799314
H,0,0.3652755486,4.1224178818,2.498941514
Cl,0,0.5527788716,4.3494381652,5.357319513
H,0,-1.2683234136,2.2228298648,6.0007330245

H,0,-2.5652236378,0.6788182092,4.5504599049
C,0,-3.677330892,0.2568555034,-3.2617403489
C,0,-1.4278017463,1.3003202343,-3.5393376791
H,0,-3.5725316682,-0.3910242739,-4.1398535591
H,0,-4.2919946484,-0.2489430858,-2.5162445229
H,0,-4.179353995,1.1818927535,-3.5588460911
H,0,-1.9618407901,1.6913507517,-4.4053867137
H,0,-0.9987638912,2.1404380131,-2.9876389991
H,0,-0.6186546516,0.6463800199,-3.8861480863
Si,0,1.8331630906,-0.5077953054,1.9774812975
C,0,3.4265691856,0.4079022382,1.6137961274
C,0,1.2703377014,-0.1870083642,3.7366965311
C,0,1.9581868903,-2.3451356572,1.6055756415
H,0,2.6838570939,-2.8193565718,2.2766764088
H,0,0.9945258649,-2.8469874534,1.7426330018
H,0,2.2876834823,-2.5138765897,0.574480655
H,0,2.076708716,-0.4567462756,4.4295857813
H,0,1.0361871602,0.8712418129,3.8831723166
H,0,0.3844460765,-0.7671293535,4.0108223126
H,0,4.2293553072,0.0630477942,2.275434532
H,0,3.7436972211,0.2491698026,0.577598974
H,0,3.2958069535,1.4841788715,1.7714320912
H,0,-3.064194739,2.7448810165,-0.016243567
C,0,-3.1600506485,3.737007755,-0.4890181801
Cl,0,-3.7464478712,4.886061089,0.7553497804
Cl,0,-1.5493561314,4.2500946298,-1.1144998204
Cl,0,-4.3372870016,3.5943599517,-1.8409099634

*m062x/6-31+g** with PCM solvent model*
scrf=(solvent=chloroform)
E(RM062X) = -1578.66837908

Zero-point correction= 0.370089 (Hartree/Particle)
Thermal correction to Energy= 0.395086
Thermal correction to Enthalpy= 0.396031
Thermal correction to Gibbs Free Energy= 0.313637
Sum of electronic and ZPE= -1578.298290
Sum of electronic and thermal Energies= -1578.273293
Sum of electronic and thermal Enthalpies= -1578.272349
Sum of electronic and thermal Free Energies= -1578.354742

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	247.920	91.227	173.411

C,0,-0.5957966,0.1557430866,-0.6889242407
C,0,-0.5270058934,-0.2028663564,0.6653299069
H,0,0.3147884985,0.5233479941,-1.1470655702
O,0,0.6635426336,0.0210659021,1.244012226
C,0,-1.6474672369,-0.5233982371,1.4714438218
C,0,-1.8078748047,0.1733515279,-1.3688673088
N,0,-1.9887519922,0.6606149697,-2.590114639
H,0,-2.6963604456,-0.2351896735,-0.9036398085
O,0,-3.1012135979,1.483884095,0.5604556341
H,0,-1.4229802983,-0.8632500395,2.4780206401
C,0,-2.5629811568,1.1502463341,1.6673365356
H,0,-2.460833936,-1.0647556797,0.9982230613
H,0,-3.2111180178,0.7372463784,2.4661899926
C,0,-1.4739917767,2.027589784,2.2411723996
C,0,-0.824681042,2.9492698144,1.418864632
C,0,0.2321835655,3.7175994504,1.9054093194
C,0,0.627761597,3.5557692456,3.2290018225
C,0,-0.0171044153,2.6586463706,4.0775204095
C,0,-1.0702635765,1.9010165791,3.5718734519
H,0,-1.1618888091,3.0484106303,0.3913008162
H,0,0.7451995763,4.4312655408,1.2692509092
Cl,0,1.9644254014,4.5047664049,3.8484528632
H,0,0.3009825922,2.5598279197,5.1103985998
H,0,-1.5830706454,1.1951821231,4.2231464481
C,0,-3.3023650604,0.6618067223,-3.2175636103
C,0,-0.9007742562,1.3165327393,-3.3007556731
H,0,-3.2661428303,0.1282921392,-4.1717216693
H,0,-4.0183061452,0.1721060145,-2.5580680652
H,0,-3.6312275229,1.6898766235,-3.3951071149
H,0,-1.2758488842,1.6897876945,-4.2530083485
H,0,-0.5155419481,2.1567828147,-2.7136438927
H,0,-0.0851412661,0.6128365199,-3.4934268817
Si,0,1.608568274,-0.8638037305,2.3465768587
C,0,2.9922350308,0.3247827999,2.7314118101
C,0,0.7032527887,-1.3463014234,3.9141637078
C,0,2.1780660124,-2.3998790029,1.443105027
H,0,2.8138267249,-3.0160498795,2.0871875194
H,0,1.3180040337,-3.0064240576,1.1394386046
H,0,2.7470912797,-2.1397021421,0.5456287934
H,0,1.4429635596,-1.7364550802,4.6230345232
H,0,0.2144951061,-0.4864189751,4.3811379355
H,0,-0.0405904117,-2.130524833,3.7471114393
H,0,3.7153510098,-0.1245677123,3.4193137269
H,0,3.5198240766,0.6191015107,1.8194323656
H,0,2.5891298083,1.2297390936,3.1990980215

Endo-DA product for the reaction of (*E*)-1-dimethylamino-3-trimethylsiloxy-1,3-butadiene with

p-chlorobenzaldehyde:
*B3lyp-d3/6-31+g** with PCM solvent model*
b3lyp/6-31+g**
EmpiricalDispersion=GD3
Scrf=(solvent=chloroform)
E(RB3LYP) = -1579.20168870

Zero-point correction= 0.371368 (Hartree/Particle)
Thermal correction to Energy= 0.395303
Thermal correction to Enthalpy= 0.396247
Thermal correction to Gibbs Free Energy= 0.317513
Sum of electronic and ZPE= -1578.830320
Sum of electronic and thermal Energies= -1578.806386
Sum of electronic and thermal Enthalpies= -1578.805442
Sum of electronic and thermal Free Energies= -1578.884175

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	248.056	89.802	165.709

C,0,-0.1963549513,-0.1898149566,-1.059399728
C,0,0.0370149577,-0.6918125259,0.161538827
H,0,0.5952828594,-0.0596749526,-1.7885763732
O,0,1.2823209796,-1.0733098134,0.5463218371
C,0,-1.1495153104,-0.8788975153,1.0731627713
C,0,-1.6187441832,0.115053871,-1.4416923194
N,0,-1.7251321972,0.9136826614,-2.6291717708
H,0,-2.1690585608,-0.8183099739,-1.6373913524
O,0,-2.3341145095,0.7840455465,-0.3394677202
H,0,-0.8552869066,-1.0335226945,2.1122166714
C,0,-2.0950585503,0.35112929,0.9986949401
H,0,-1.7062106144,-1.7733769201,0.7625449121
H,0,-3.0611526085,0.0452588861,1.4223767187
C,0,-1.5546088123,1.4981740008,1.838458724
C,0,-0.6918451473,2.4575153946,1.2968454121
C,0,-0.1371911414,3.4583806513,2.0971189757
C,0,-0.4548861922,3.4945810753,3.4542684276
C,0,-1.3240186724,2.5611692374,4.0195444169
C,0,-1.8705172616,1.5700099993,3.2015848624
H,0,-0.4527848226,2.418049647,0.242090908
H,0,0.535730706,4.1958963192,1.6733605321
Cl,0,0.2491458237,4.7505152999,4.4762464956
H,0,-1.5705186158,2.6096061906,5.0744997675
H,0,-2.5484100201,0.8407612659,3.6387481433
C,0,-3.0862984581,0.9888109257,-3.1626544682
C,0,-1.1079001,2.2393356097,-2.5452780063
H,0,-3.0560161803,1.4296453438,-4.1641519339
H,0,-3.5069242824,-0.0179312834,-3.2456738261

H,0,-3.757872954,1.5969809134,-2.5356494874
H,0,-1.0746372409,2.6791893339,-3.5467501556
H,0,-1.6621881628,2.9225014141,-1.8828613559
H,0,-0.0821652076,2.1577475412,-2.1777075538
Si,0,2.0589131708,-1.2005726378,2.0558262985
C,0,3.8535664276,-1.4667408791,1.583771513
C,0,1.8232601094,0.3875085716,3.0288036011
C,0,1.3955321264,-2.6894036247,2.9986624725
H,0,2.0288183469,-2.8861996683,3.8723133814
H,0,0.3724147179,-2.5396258377,3.3584959088
H,0,1.4075161151,-3.5846469367,2.3668699817
H,0,2.4042520567,0.3467824861,3.9580068699
H,0,2.1650761367,1.2534876453,2.4527867808
H,0,0.776326712,0.5607007978,3.2951137304
H,0,4.4743443573,-1.5856474944,2.4792564747
H,0,3.9663243977,-2.3668319929,0.9695681332
H,0,4.2368706631,-0.6137742116,1.0133535622

*B3lyp-d3/6-31+g** with PCM solvent model and an explicit $CHCl_3$ molecule*
b3lyp/6-31+g**
EmpiricalDispersion=GD3
Scrf=(solvent=chloroform)
E(RB3LYP) = -2998.48969094

Zero-point correction= 0.387713 (Hartree/Particle)
Thermal correction to Energy= 0.419465
Thermal correction to Enthalpy= 0.420409
Thermal correction to Gibbs Free Energy= 0.319816
Sum of electronic and ZPE= -2998.101977
Sum of electronic and thermal Energies= -2998.070226
Sum of electronic and thermal Enthalpies= -2998.069282
Sum of electronic and thermal Free Energies= -2998.169875

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	263.218	111.531	211.716

C,0,-0.7602066174,0.2518814715,-0.9051649847
C,0,-0.4723838642,-0.1855690077,0.4043135461
H,0,0.0410007865,0.7645118836,-1.4243780641
O,0,0.7479077064,0.1800715625,0.842909424
C,0,-1.405269604,-0.7959349875,1.2818111367
C,0,-2.0097408618,0.1042521766,-1.491861314
N,0,-2.3661571406,0.5633070964,-2.69507509
H,0,-2.7927842466,-0.4189747384,-0.9592627382
O,0,-3.2582517113,1.0994664756,0.7870686344
H,0,-1.0119611481,-1.188633519,2.214084458
C,0,-2.68555624,0.6199064424,1.8313970342

H,0,-2.1489254579,-1.4398967354,0.8232718854
H,0,-3.2591826518,-0.1038294604,2.4405929053
C,0,-1.8503395374,1.5277109359,2.7015809903
C,0,-1.021291821,2.5068326151,2.1382954726
C,0,-0.2801143231,3.3714711629,2.9415292726
C,0,-0.3812984748,3.2571285669,4.3298765739
C,0,-1.2005543338,2.295987091,4.9208013811
C,0,-1.926119269,1.4321752409,4.0962166684
H,0,-0.9424406281,2.5819622995,1.0606799314
H,0,0.3652755486,4.1224178818,2.498941514
Cl,0,0.5527788716,4.3494381652,5.357319513
H,0,-1.2683234136,2.2228298648,6.0007330245
H,0,-2.5652236378,0.6788182092,4.5504599049
C,0,-3.677330892,0.2568555034,-3.2617403489
C,0,-1.4278017463,1.3003202343,-3.5393376791
H,0,-3.5725316682,-0.3910242739,-4.1398535591
H,0,-4.2919946484,-0.2489430858,-2.5162445229
H,0,-4.179353995,1.1818927535,-3.5588460911
H,0,-1.9618407901,1.6913507517,-4.4053867137
H,0,-0.9987638912,2.1404380131,-2.9876389991
H,0,-0.6186546516,0.6463800199,-3.8861480863
Si,0,1.8331630906,-0.5077953054,1.9774812975
C,0,3.4265691856,0.4079022382,1.6137961274
C,0,1.2703377014,-0.1870083642,3.7366965311
C,0,1.9581868903,-2.3451356572,1.6055756415
H,0,2.6838570939,-2.8193565718,2.2766764088
H,0,0.9945258649,-2.8469874534,1.7426330018
H,0,2.2876834823,-2.5138765897,0.574480655
H,0,2.076708716,-0.4567462756,4.4295857813
H,0,1.0361871602,0.8712418129,3.8831723166
H,0,0.3844460765,-0.7671293535,4.0108223126
H,0,4.2293553072,0.0630477942,2.275434532
H,0,3.7436972211,0.2491698026,0.577598974
H,0,3.2958069535,1.4841788715,1.7714320912
H,0,-3.064194739,2.7448810165,-0.016243567
C,0,-3.1600506485,3.737007755,-0.4890181801
Cl,0,-3.7464478712,4.886061089,0.7553497804
Cl,0,-1.5493561314,4.2500946298,-1.1144998204
Cl,0,-4.3372870016,3.5943599517,-1.8409099634

*m062x/6-31+g** with PCM solvent model*
scrf=(solvent=chloroform)
E(RM062X) = -1578.66837908

Zero-point correction= 0.370089 (Hartree/Particle)
Thermal correction to Energy= 0.395086
Thermal correction to Enthalpy= 0.396031
Thermal correction to Gibbs Free Energy= 0.313637

Sum of electronic and ZPE= -1578.298290
Sum of electronic and thermal Energies= -1578.273293
Sum of electronic and thermal Enthalpies= -1578.272349
Sum of electronic and thermal Free Energies= -1578.354742

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	247.920	91.227	173.411

C,0,-0.5957966,0.1557430866,-0.6889242407
C,0,-0.5270058934,-0.2028663564,0.6653299069
H,0,0.3147884985,0.5233479941,-1.1470655702
O,0,0.6635426336,0.0210659021,1.244012226
C,0,-1.6474672369,-0.5233982371,1.4714438218
C,0,-1.8078748047,0.1733515279,-1.3688673088
N,0,-1.9887519922,0.6606149697,-2.590114639
H,0,-2.6963604456,-0.2351896735,-0.9036398085
O,0,-3.1012135979,1.483884095,0.5604556341
H,0,-1.4229802983,-0.8632500395,2.4780206401
C,0,-2.5629811568,1.1502463341,1.6673365356
H,0,-2.460833936,-1.0647556797,0.9982230613
H,0,-3.2111180178,0.7372463784,2.4661899926
C,0,-1.4739917767,2.027589784,2.2411723996
C,0,-0.824681042,2.9492698144,1.418864632
C,0,0.2321835655,3.7175994504,1.9054093194
C,0,0.627761597,3.5557692456,3.2290018225
C,0,-0.0171044153,2.6586463706,4.0775204095
C,0,-1.0702635765,1.9010165791,3.5718734519
H,0,-1.1618888091,3.0484106303,0.3913008162
H,0,0.7451995763,4.4312655408,1.2692509092
Cl,0,1.9644254014,4.5047664049,3.8484528632
H,0,0.3009825922,2.5598279197,5.1103985998
H,0,-1.5830706454,1.1951821231,4.2231464481
C,0,-3.3023650604,0.6618067223,-3.2175636103
C,0,-0.9007742562,1.3165327393,-3.3007556731
H,0,-3.2661428303,0.1282921392,-4.1717216693
H,0,-4.0183061452,0.1721060145,-2.5580680652
H,0,-3.6312275229,1.6898766235,-3.3951071149
H,0,-1.2758488842,1.6897876945,-4.2530083485
H,0,-0.5155419481,2.1567828147,-2.7136438927
H,0,-0.0851412661,0.6128365199,-3.4934268817
Si,0,1.608568274,-0.8638037305,2.3465768587
C,0,2.9922350308,0.3247827999,2.7314118101
C,0,0.7032527887,-1.3463014234,3.9141637078
C,0,2.1780660124,-2.3998790029,1.443105027
H,0,2.8138267249,-3.0160498795,2.0871875194
H,0,1.3180040337,-3.0064240576,1.1394386046
H,0,2.7470912797,-2.1397021421,0.5456287934

H,0,1.4429635596,-1.7364550802,4.6230345232
H,0,0.2144951061,-0.4864189751,4.3811379355
H,0,-0.0405904117,-2.130524833,3.7471114393
H,0,3.7153510098,-0.1245677123,3.4193137269
H,0,3.5198240766,0.6191015107,1.8194323656
H,0,2.5891298083,1.2297390936,3.1990980215

POLYRATE sample input files

p.dat:

```
*General

  TITLE
Hetero-Diels-Alder
END

 ATOMS
   1  C
   2  C
   3  H
   4  O
   5  C
   6  C
   7  N
   8  H
   9  O
  10  H
  11  C
  12  H
  13  H
  14  C
  15  C
  16  C
  17  C
  18  C
  19  C
  20  H
  21  H
  22  Cl
  23  H
  24  H
  25  C
  26  C
  27  H
  28  H
  29  H
  30  H
  31  H
  32  H
```

```
 33  Si
 34  C
 35  C
 36  C
 37  H
 38  H
 39  H
 40  H
 41  H
 42  H
 43  H
 44  H
 45  H
 46  H
 47  C
 48  Cl
 49  Cl
 50  Cl
END

NOSUPERMOL

WRITEFU31 ON
INPUNIT AU

*OPTIMIZATION

OPTMIN  OHOOK
OPTTS   OHOOK

*SECOND

HESSCAL HHOOK

*REACT1
SPECIES   NONLINRP
INITGEO  HOOKS
GEOM
 1
 2
 3
 4
 5
 6
 7
 8
 9
 10
```

```
 11
 12
 13
 14
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 36
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 39
 40
 41
 42
 43
 44
 45
 46
 47
 48
 49
 50
END

*PROD1
SPECIES   NONLINRP
INITGEO  HOOKS
GEOM
  1
  2
```

```
 END

*START
 SPECIES NONLINTS
 INITGEO  HOOKS
 GEOM
  1
  2
  3
  4
  5
  6
  7
  8
  9
 10
 11
 12
 13
 14
 15
 16
 17
 18
 19
 20
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 38
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 41
 42
```

```
  43
  44
  45
  46
  47
  48
  49
  50
 END

# end of start section

*PATH

 SCALEMASS  1.00

RODS ON

 INTMU   3
 SSTEP   0.01
 INH     10

 SRANGE

  SLP   7.50
  SLM  -0.40
 END

 RPM       pagem

 SIGN    PRODUCT

 IDIRECT   1

 COORD  CART

 FREQSCALE 1.000000

 PRPATH
  COORD 2 4
  INTERVAL 1
  XMOL
 END

#SPECSTOP
# CURVE vag
# POINT savegrid
# PERCENTDOWN 95.
```

```
#END

*TUNNEL

QUAD
 NQE   40
 NQTH  40
END

 SCT

*RATE

  FORWARDK

  SIGMAF       1
  CVT
  PRDELG ON
# PRGIGT ON

  TEMP
    273.15
    298.15
    323.15
    350
  END
```

p.70:

```
*GRGENERAL

  GRRESTART
  RSTTOL 0.00001

*GRSTART

  CHARGE      0
  MULTIPLICITY  1

*GRREACT1

  CHARGE      0
  MULTIPLICITY  1

*GRPROD1

  CHARGE      0
  MULTIPLICITY  1
```

```
*GRCOMMON

 GRENER
    #p B3LYP/6-31+G** FCHK SYMM=none UNITS=AU
    scf=tight
    int(grid=ultrafine)
    scrf=(solvent=chloroform)
    EmpiricalDispersion=GD3
 END

 GRFIRST
    #p B3LYP/6-31+G** FORCE FCHK NOSYMM UNITS=AU
    scf=tight
    int(grid=ultrafine)
    scrf=(solvent=chloroform)
    EmpiricalDispersion=GD3
 END

 GRSEC
    #p B3LYP/6-31+G** FREQ=NORAMAN FCHK NOSYMM UNITS=AU
    scf=tight
    int(grid=ultrafine)
    scrf=(solvent=chloroform)
    EmpiricalDispersion=GD3
 END

 GRLINK0
   %chk=g09.chk
   %nproc=20
   %mem=40gb
 END
```

p.71:

```
%nproc=20
%mem=40gb
%chk=g09.chk
#p B3LYP/6-31+G** opt fchk SYMMETRY=None
scf=tight int(grid=ultrafine)
scrf=(solvent=chloroform)
EmpiricalDispersion=GD3

Diels-Alder

0 1
 C,0,-0.8814503153,0.3525477438,-0.4049977234
 C,0,-0.6704127704,-0.2439808513,0.9056006736
 H,0,-0.02546671,0.8731890989,-0.8198876096
 O,0,0.4283614968,0.2921294699,1.5288812858
```

C,0,-1.4545666563,-1.1713329723,1.5131384491
C,0,-2.0754435791,0.3201644333,-1.065472953
N,0,-2.3261411741,0.7806516385,-2.3231676635
H,0,-2.9416641737,-0.1145899013,-0.5769741791
O,0,-3.859778209,1.3977260557,1.1830601635
H,0,-1.2703047512,-1.4871842103,2.5314422954
C,0,-3.2593732362,1.2011347474,2.2387248053
H,0,-2.2804992733,-1.6304604296,0.984488243
H,0,-3.5929379857,0.4003768349,2.922842447
C,0,-2.1179965594,2.0022993584,2.7104254315
C,0,-1.4647846105,2.9031916578,1.8552204313
C,0,-0.3899083192,3.6576011613,2.3124944177
C,0,0.0259964244,3.5036347864,3.6374898667
C,0,-0.6031623205,2.6100325711,4.5082303334
C,0,-1.6728288941,1.8555449722,4.0323481062
H,0,-1.778436269,2.9801106818,0.8223251604
H,0,0.127586695,4.3447707608,1.6528879689
Cl,0,1.3915299321,4.4458381226,4.2219317098
H,0,-0.2552075625,2.5051559249,5.5295553348
H,0,-2.1636247425,1.1451815889,4.6924000096
C,0,-3.7006096312,1.017846977,-2.7497998196
C,0,-1.2769428166,1.4530315618,-3.0723709529
H,0,-3.8190404909,0.7395984612,-3.801998365
H,0,-4.381928811,0.4102628163,-2.1505443361
H,0,-3.9865651376,2.0714271336,-2.6351617713
H,0,-1.6163474666,1.6201175542,-4.0965124672
H,0,-1.0155004466,2.4236652463,-2.6262086274
H,0,-0.3766361757,0.8306564348,-3.1011001547
Si,0,1.6194816027,-0.4340211919,2.4919628661
C,0,2.8879243475,0.9330813059,2.6964802839
C,0,0.9537996147,-0.954952703,4.1758147226
C,0,2.3087960364,-1.9183588762,1.5660907127
H,0,3.0841062975,-2.4192009225,2.1577009697
H,0,1.5174181585,-2.6465425122,1.3576662381
H,0,2.7512419458,-1.6126840559,0.6115136236
H,0,1.7917576549,-1.1649660466,4.8518707256
H,0,0.3535143909,-0.1551053488,4.6206249477
H,0,0.338571264,-1.8586584255,4.1178815267
H,0,3.7383599664,0.5885886187,3.2961451971
H,0,3.266674424,1.2626506409,1.7228677479
H,0,2.4465514838,1.7999820521,3.1992407779
H,0,-4.0587329207,3.1084726699,0.1455192406
C,0,-4.2274528811,4.1080910397,-0.2589569131
Cl,0,-4.3108698474,5.2430033552,1.1246025633
Cl,0,-2.8443664075,4.5091812289,-1.336740268
Cl,0,-5.7667825904,4.0862437422,-1.1777494726

p.73:

%mem=40gb
%chk=g09.chk
#p B3LYP/6-31+G** opt=loose fchk SYMMETRY=None
scf=tight int(grid=ultrafine)
scrf=(solvent=chloroform)
EmpiricalDispersion=GD3

Hetero-Diels-Alder

0 1
C,0,-0.1966914279,-0.2445304341,-1.1030708237
C,0,0.0412620018,-0.7073780951,0.1330498207
H,0,0.5983851584,-0.1007348017,-1.8257995968
O,0,1.2953641878,-1.0229780323,0.5427774314
C,0,-1.1473959641,-0.9093216132,1.0391304515
C,0,-1.6220806521,0.0038926623,-1.5104625723
N,0,-1.7451479929,0.7727498763,-2.7107168686
H,0,-2.1458614104,-0.9476560933,-1.6825714406
O,0,-2.3745128545,0.6745714925,-0.420241463
H,0,-0.8595497006,-1.0366117785,2.0834568286
C,0,-2.1190061614,0.2934157263,0.9358342622
H,0,-1.6804348795,-1.8221286542,0.7411626158
H,0,-3.0781421355,-0.0166454025,1.3686349952
C,0,-1.6088008822,1.4877556891,1.725331596
C,0,-0.7061320089,2.4003117208,1.1673578036
C,0,-0.1986161894,3.4597801645,1.9196817047
C,0,-0.6069483282,3.6049629733,3.2446093131
C,0,-1.5155913322,2.7194557627,3.8241242959
C,0,-2.0122523157,1.6663770298,3.0541594476
H,0,-0.4011020557,2.2823745359,0.1357123945
H,0,0.5010427147,4.1634288215,1.4822295707
Cl,0,0.0276192586,4.943370821,4.2040571988
H,0,-1.8351327892,2.855629717,4.8513045297
H,0,-2.7293591253,0.9806206543,3.4977618026
C,0,-3.0955053589,0.7728903156,-3.2771617452
C,0,-1.1769265362,2.1206218283,-2.6545337861
H,0,-3.0604340493,1.1907564943,-4.2881243332
H,0,-3.4668888411,-0.2539239859,-3.3448656993
H,0,-3.810473918,1.3642570212,-2.6855762733
H,0,-1.1558813767,2.5396385179,-3.6648039443
H,0,-1.7556971473,2.8023857957,-2.0115025215
H,0,-0.15088738,2.085417412,-2.2810209265
Si,0,2.0375748471,-1.1330458765,2.0727437601
C,0,3.8526423038,-1.3202834863,1.6447489153
C,0,1.7150195379,0.4359084289,3.0526121812
C,0,1.4093693135,-2.6566017348,2.9828686594
H,0,2.0295935414,-2.8396941853,3.8687467978
H,0,0.3733847341,-2.550254251,3.3205509081

H,0,1.4700978285,-3.5430351209,2.3415780736
H,0,2.27222146,0.4059231004,3.9966620058
H,0,2.0415750035,1.3188660183,2.4938774001
H,0,0.6559732307,0.5712066215,3.2920880997
H,0,4.4546640626,-1.4175997884,2.5555276395
H,0,4.019213528,-2.2113427575,1.0296723877
H,0,4.2136716798,-0.4485289534,1.0884394411
H,0,-3.4661246356,2.4414599138,-0.2210962871
C,0,-4.2956245893,3.0644880108,0.1146087295
Cl,0,-5.311322588,2.0483389088,1.1917729962
Cl,0,-3.63864343,4.4772872309,0.9918300984
Cl,0,-5.2208293361,3.5793447789,-1.3365458747

p.75:

```
%nproc=20
%mem=40gb
%chk=g09.chk
#p B3LYP/6-31+G** opt=(ts,calcfc,noeigentest) fchk SYMMETRY=None
int(grid=ultrafine)
scrf=(solvent=chloroform)
EmpiricalDispersion=GD3

hetero Diels-Alder

0 1
C,0,-0.7602066174,0.2518814715,-0.9051649847
C,0,-0.4723838642,-0.1855690077,0.4043135461
H,0,0.0410007865,0.7645118836,-1.4243780641
O,0,0.7479077064,0.1800715625,0.842909424
C,0,-1.405269604,-0.7959349875,1.2818111367
C,0,-2.0097408618,0.1042521766,-1.491861314
N,0,-2.3661571406,0.5633070964,-2.69507509
H,0,-2.7927842466,-0.4189747384,-0.9592627382
O,0,-3.2582517113,1.0994664756,0.7870686344
H,0,-1.0119611481,-1.188633519,2.214084458
C,0,-2.68555624,0.6199064424,1.8313970342
H,0,-2.1489254579,-1.4398967354,0.8232718854
H,0,-3.2591826518,-0.1038294604,2.4405929053
C,0,-1.8503395374,1.5277109359,2.7015809903
C,0,-1.021291821,2.5068326151,2.1382954726
C,0,-0.2801143231,3.3714711629,2.9415292726
C,0,-0.3812984748,3.2571285669,4.3298765739
C,0,-1.2005543338,2.295987091,4.9208013811
C,0,-1.926119269,1.4321752409,4.0962166684
H,0,-0.9424406281,2.5819622995,1.0606799314
H,0,0.3652755486,4.1224178818,2.498941514
Cl,0,0.5527788716,4.3494381652,5.357319513
H,0,-1.2683234136,2.2228298648,6.0007330245
```

H,0,-2.5652236378,0.6788182092,4.5504599049
C,0,-3.677330892,0.2568555034,-3.2617403489
C,0,-1.4278017463,1.3003202343,-3.5393376791
H,0,-3.5725316682,-0.3910242739,-4.1398535591
H,0,-4.2919946484,-0.2489430858,-2.5162445229
H,0,-4.179353995,1.1818927535,-3.5588460911
H,0,-1.9618407901,1.6913507517,-4.4053867137
H,0,-0.9987638912,2.1404380131,-2.9876389991
H,0,-0.6186546516,0.6463800199,-3.8861480863
Si,0,1.8331630906,-0.5077953054,1.9774812975
C,0,3.4265691856,0.4079022382,1.6137961274
C,0,1.2703377014,-0.1870083642,3.7366965311
C,0,1.9581868903,-2.3451356572,1.6055756415
H,0,2.6838570939,-2.8193565718,2.2766764088
H,0,0.9945258649,-2.8469874534,1.7426330018
H,0,2.2876834823,-2.5138765897,0.574480655
H,0,2.076708716,-0.4567462756,4.4295857813
H,0,1.0361871602,0.8712418129,3.8831723166
H,0,0.3844460765,-0.7671293535,4.0108223126
H,0,4.2293553072,0.0630477942,2.275434532
H,0,3.7436972211,0.2491698026,0.577598974
H,0,3.2958069535,1.4841788715,1.7714320912
H,0,-3.064194739,2.7448810165,-0.016243567
C,0,-3.1600506485,3.737007755,-0.4890181801
Cl,0,-3.7464478712,4.886061089,0.7553497804
Cl,0,-1.5493561314,4.2500946298,-1.1144998204
Cl,0,-4.3372870016,3.5943599517,-1.8409099634

List of dynamic programs for Program Suite PROGDYN

A full listing of the subprograms of PROGDYN is given below. To allow the reader to understand or make use of PROGDYN, we describe here first the overall structure of the program. We also list and describe in this section a number of helper programs that were used to analyze the data from the trajectory calculations.

The master control program for dynamics, in the form of a Unix Shell Script, is called *progdynstarterHP*. For a user to start to use *progdynstarterHP*, some early lines in it that assign the scratch space and the location of the program files and input files would have to be modified for the local environment. These lines are between lines 45 and 55 and should be apparent. The location of the scratch space is usually passed to *progdynstarterHP* as a parameter.

progdynstarterHP takes as input files:

freqinHP - This is the standard output from a Gaussian 98, 03, or 09 frequency calculation using freq=hpmodes. For isotopically labeled compounds, use freq=(hpmodes,readisotopes).

progdyn.conf – This is a file giving a variety of configuration options, called on by many of the subprograms. progdyn.conf examples are listed below and contains explanations of the program options.

isomernumber - A number in file isomernumber provides a start for numbering runs. The default is 1.

detour – A signal file that, by existing, signals the program to do a side calculations

nogo – A signal file that, by existing, signals the program to stop between points

bypassproggen - A signal file that, by existing, signals the program to use a supplied input file *geoPlusVel* instead of generating one for itself. This pathway for initialization is important here because it is used when the program progdynsam, described later, is used to generate the geoPlusVel file.

methodfile – A file that contains lines to be added to the end of each g09.com input file, such as lines that call for an NMR calculation

ZMAT – An input file for the CFOUR (http://www.cfour.de) suite of programs. When ZMAT is supplied, *progdynstarterHP* will automatically run call CFOUR (which must be set up independently by the user) by making use of the script *progcfour*.

cannontraj – A file containing a vector for each atom, used to fire an initial geometry in a particular direction.

progdynstarterHP calls the following programs:
proggenHP - An awk program that starts a trajectory, giving each mode its zero point energy (if a quasiclassical calculation) plus random additional excitations depending on the temperature.

prog1stpoint – Awk program that creates the first Gaussian input file for each run

prog2ndpoint – Awk program that creates the second Gaussian input file for each run. prog2ndpoint also checks the energy of the first point to see if it fits with the desired energy, and aborts the run if it does not by creating appropriate output in file Echeck

progdynb – Creates subsequent Gaussian input files until run is completed, written in awk

proganal – A program to analyze the latest point and see if a run is done. This program must be redone for each new system. Elaborate changes are sometimes programmed into proganal, such as the automatic changing of configuration variables. proganal creates the output to dynfollowfile and NMRlist or NMRlistdis

randgen – A program that generates random numbers between 0 and 1. These are generated all at once and stored in a file for use by proggenHP.

progcfour – A control script to run CFOUR calculations (not needed for most kinds of runs).

progdynstarterHP has the following output files:

isomernumber – A running tab of the trajectory number

runpointnumber – a running tab of the point in the trajectory

Echeck – output form where prog2ndpoint checks the energy of the trajectory to see if it fits with the desired energy

geoRecord – A record of all of the geoPlusVel files.

geoPlusVel – Created by proggen, this gives the starting positions, velocities, isotopic masses, excitations of the normal modes, and initial displacements of the normal modes for current run.
g09.com – Created by prog1stpoint, prog2ndpoint, and progdynb, this is the latest input file for Gaussian09 for current run and latest point.

olddynrun, *olddynrun2, olddynrun3* – files containing the last three outputs from Gaussian, for creation of the next point

traj, traj1, traj2, traj3, etc. – files containing the geometries and energies for each trajectory, numbered by the isomernumber, in a format suitable for reading by Molden.

dynfollowfile – A short record of the runs and their results. The data desired for *dynfollowfile* must be programed into the script *proganal* as needed for each system studied.

NMRlist or *NMRlistdis* – output of NMR predictions at each point in a trajectory, when desired

skipstart - A signal file that, by existing, tells progdynstarterHP that we are in the middle of a run. For trajectories that are propagated forward and backward in time, skipstart keeps track of whether one is in the forward or reverse part.
diagnostics – optional output that follows which subprograms are running and configuration variables, decided by variable in progdyn.conf

vellist – optional output that lists the velocities of each atom, decided by variable in progdyn.conf, or lists the total kinetic energy in the system and the classical temperature, often also keeps track of the density
A number of files starting with *'temp'* are created then later erased.

The following helper programs were used for the nitration study:
progdynsam – an awk program that generates a geoPlusVel file based on input from a *traj* file. Typically, the traj file is a trajectory performed with constraints, and the new geoPlusVel will be started without constraints. *progdynsam* must be modified for the desired temperature, and it takes as input the variable pt to decide which points in the traj file are used to define the geoPlusVel. For previously constrained atoms, *progdynsam* gives the atoms a Boltzmann-random velocity and direction of motion appropriate for the desired temperature. The program is invoked with awk –v pt=## –f progdynsam traj where ## is the trajectory point used to start a new geoPlusVel, and traj is the output file from above containing the list of trajectory points.

progwhere – an awk program used to analyze the output data in *dynfollowfile*. It is involked with awk –f progtrajlength dynfollowfile where dynfollowfile is a list of one or more of the dynfollowfile output files described above.

whamnit – a shell script that extracts data from the dynfollowfile files, sets up and runs wham to calculate the PMF, and keeps track of some general aspects of trajectories

progseries – an AWK script used by whamnit to extract data from the dynfollowfile files

wham – a program from Grossfield, Alan, "WHAM: the weighted histogram analysis method", version 2.0.9, http://membrane.urmc.rochester.edu/content/wham that performs the wham analysis

prog3dpath – a program that takes the output from dynfollowfile and generates the data for a 3d path relative to the aveage position of the arene carbons, used for generating the the pictures in Figure 2 of the paper.

nitrationPara1.m – This is an example of the Matlab version 2014 b code that was used to generate along with the data from prog3dpath to generate the Figures in Figure 2.

Program progdynstarterHP

```
#!/bin/bash
#progdynstarterHP, made to use high-precision modes from Gaussian output with freq=hpmodes
#updated to create a random number file temp811 that is used by proggenHP
#version September 16, 2005, made for workstations
#version August 2007 to allow periodic copying of g09.log to dyn putting it under control of progdynb
#version Feb 2008 moves variables like the scratch directory and location of randgen to the
```

```
beginning
#version March 2008 added proganal reporting to points 1 and 2
#version Jan 2009 fixed bug generator of having proganal run twice in checking for complete runs
#version May 2009 Echeck catches bad energies after only one point, other lines written simpler, triple while loop, revised comments
#version Aug 2010 isomernumber adds words to ease parsing, increased elements up to bromine, runpointnumber checked for more appropriate restarts
#version Aug 2011 runpointnumber starts better, restart better if died during first few points, awk bug fix
#version Aug 2012 freqinHP reads with only 3 freqs, goingwell and other temp files moved to $scratchdir
#version Aug 2013 adds ability to automatically run a CFOUR program if the file ZMAT exists
#
#version Nov 2013 adds ability to bypass generation of geoPlusVel using the signal file bypassproggen
#version Nov 2015 makes using guess=read easier, improves ability to restart after disk write failures, partially allows for MM runs in Gaussian
#LIMITATIONS - standard version only handles elements up to bromine, must change program to do higher atomic numbers
#  only handles up to 4000th excited state for modes - this could start to affect the initialization of classical modes or transition vectors at
#  extremely high temperatures
#  The routine that checks whether the actual energy approximately equals the desired energy checks for lines containing "SCF Done" or "EUMP2 =" or " Energy="
#  This should handle ordinary calculations HF, DFT, ONIOM, and MP2 calculatons but the routine in prog2ndpoint would have to be changed for other calcs.
#
#                                   OUTLINE
# A. initilize to perform Gaussian jobs, set the scratch, program, and other directores, remove errant control files
#  start outermost loop L1L1L1L1L1L1L1L1
#  start loop 2 L2L2L2L2L2L2L2L2
# B. branch on whether there is a file named "skipstart"
#  if there is, skip B1, B2, B3 entirely
#  if no file named "skipstart" then generate a new isomer.  Instructions: Get rid of skipstart to start new isomer.
#  the B loop generates geoPlusVel, adds it to geoRecord, generates and runs first and second points, and sets up for continuous loop
#  B1. generates geoPlusVel, isomernumber, runpointnumber=1, then makes g09.com for point 1
#  B2. checks for success of B1 or exits, then sets geoRecord then runs g09.com.  Checks for its success or exits.
#  B3. runpointnumber=2, kills run if XXXX in dynfollowfile due to bad energy probably, makes g09.com for point 2, runs it
#    checks for its success or exits
#    runpointnumber=3, uses progdynb to make g09.com for point 3
#    sets skipstart=forward
#     B4.  Only  runs  if  skipstart=ireverserestart,  performs  reverserestart,  ends  with
```

```
runpointnumber=3
#      sets skipstart=reverse
# C. loop over propagation steps
#
#
AAAA
```

```
#### Triple 'while' loop - will have to break multiple times to get out, but advantage is ability to control starting over
#L1L1L1
```

```
    fi
    if (test -f isomernumber) then
      cp isomernumber temp533
      awk 'BEGIN {getline;i=$1+1;print i,"----trajectory isomer number----"}' temp533 >
isomernumber
      rm temp533
    else
      echo "1 ----trajectory isomer number----" > isomernumber
    fi
    echo 1 > runpointnumber
    rm g09.com
    awk -f $proggramdir/prog1stpoint isomernumber > g09.com
#   B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2
if first part successfule then clean up and run the first input file, otherwise die
    if (test -s g09.com) then
      rm tempfreqs tempredmass tempfrc tempmodes tempstangeos tempmasses temp401
temp811 tempinputgeos
      cat isomernumber >> geoRecord
      cat geoPlusVel >> geoRecord
      rm -f $scratchdir/goingwell
      cd $scratchdir
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      cd $origdir
      grep 'Normal termination' $scratchdir/g09.log > $scratchdir/goingwell
      if (test -s $scratchdir/goingwell) then
        cp $scratchdir/g09.log olddynrun2
      else
        cp $scratchdir/g09.log $origdir/g09.log
        break
      fi
    else
      break
    fi
#   B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3
if B2 worked then you are here.  create 2nd point, run it, and set up for propagation loop
    rm g09.com
    echo 2 > runpointnumber
    awk -f $proggramdir/prog2ndpoint $scratchdir/g09.log > g09.com
# before we decide to run this, check the energy
    awk -f $proggramdir/proganal $scratchdir/g09.log >> dynfollowfile
    rm -f $scratchdir/tempdone
    tail -1 dynfollowfile | awk '/XXXX/ {print}' > $scratchdir/tempdone
    if (test  -s $scratchdir/tempdone) then
      rm -f dyn
      rm -f traj
      echo 0 > runpointnumber
      break
```

```
    fi
    if (test -s g09.com) then
      rm -f $scratchdir/goingwell
      cd $scratchdir
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      cd $origdir
      grep 'Normal termination' $scratchdir/g09.log > $scratchdir/goingwell
      if (test -s $scratchdir/goingwell) then
        cp $scratchdir/g09.log olddynrun
        awk -f $proggramdir/proganal $scratchdir/g09.log >> dynfollowfile
        awk '/Input orientation/,/Distance matrix/ {print};/Matrix orientation/,/Stoichiometry/
{print}' olddynrun | awk '{if (($2>.5) && ($2<100)) print}' > old
        awk '/Input orientation/,/Distance matrix/ {print};/Matrix orientation/,/Stoichiometry/
{print}' olddynrun2 | awk '{if (($2>.5) && ($2<100)) print}' > older
        echo 3 > runpointnumber
        if (test -f bypassproggen) then
          cat bypassproggen > runpointnumber
          echo 3 > bypassproggen
        fi
        awk -f $proggramdir/progdynb olddynrun > g09.com
        rm -f old older
      else
        cp $scratchdir/g09.log $origdir/g09.log
        break
      fi
    else
      break
    fi
# we've just completed a start, so lets skipstart until instructed otherwise
    echo "forward" > skipstart
  fi
#
B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4
B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4
B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4
# Reverse trajectories starter routine
  if [ `cat skipstart` = "reverserestart" ]; then
    cd $origdir
    rm g09.com
    echo 1 > runpointnumber
    awk -f $proggramdir/prog1stpoint isomernumber > g09.com
    if (test -s g09.com) then
      rm -f $scratchdir/goingwell
      cd $scratchdir
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      cd $origdir
```

```
      grep 'Normal termination' $scratchdir/g09.log > $scratchdir/goingwell
      if (test -s $scratchdir/goingwell) then
        cp $scratchdir/g09.log olddynrun2
      else
        cp $scratchdir/g09.log $origdir/g09.log
        break
      fi
    else
      break
    fi
    rm g09.com
    echo 2 > runpointnumber
    awk -f $proggramdir/prog2ndpoint $scratchdir/g09.log > g09.com
    awk -f $proggramdir/proganal $scratchdir/g09.log >> dynfollowfile
    rm -f $scratchdir/tempdone
    if (test -s g09.com) then
      rm -f $scratchdir/goingwell
      cd $scratchdir
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      cd $origdir
      grep 'Normal termination' $scratchdir/g09.log > $scratchdir/goingwell
      if (test -s $scratchdir/goingwell) then
        cp $scratchdir/g09.log olddynrun
        cat $scratchdir/g09.log >> dyn
        awk -f $proggramdir/proganal $scratchdir/g09.log >> dynfollowfile
        awk '/Input orientation/,/Distance matrix/ {print};/Matrix orientation/,/Stoichiometry/
{print}' olddynrun | awk '{if (($2>.5) && ($2<100)) print}' > old
        awk '/Input orientation/,/Distance matrix/ {print};/Matrix orientation/,/Stoichiometry/
{print}' olddynrun2 | awk '{if (($2>.5) && ($2<100)) print}' > older
        echo 3 > runpointnumber
        if (test -f bypassproggen) then
          cat bypassproggen > runpointnumber
        fi
        awk -f $proggramdir/progdynb olddynrun > g09.com
        rm -f old older
      else
        cp $scratchdir/g09.log $origdir/g09.log
        break
      fi
    else
      break
    fi
# we've just completed a reversestart, so lets skipstart until instructed otherwise
    echo "reverse" > skipstart
  fi

#
```

```
END_of_B___END_of_B___END_of_B___END_of_B___END_of_B___END_of_B___END_
of_B___END_of_B___

#
CCCC
```

```
    fi

# here is a cool link that lets you interupt the dynamics with a short job, then
# it automatically goes back to the dynamics  just make the file 'detour' and it
# will delete detour, run run.com, then go back to dynamics
    if (test  -f detour) then
      rm detour
      date >> $logfile
      cat run.com >> $logfile
      cp run.log temp.log
      cd $scratchdir
      $g09root/g09/g09 $origdir/run.com > $origdir/run.log
      cd $origdir
    fi

#stop it all nicely by creating a nogo file
    if (test  -f nogo) then
      break
    fi

#figure out if this isomer is done - change in april 2013 is to move proganal call up from here
    rm -f $scratchdir/tempdone
    tail -2 dynfollowfile | awk '/XXXX/ {print}' > $scratchdir/tempdone
    if (test  -s $scratchdir/tempdone) then
      if [ `awk '/reversetraj/ {if ($1=="reversetraj") print $2}' progdyn.conf` = "true" ]; then
        if [ `cat skipstart` = "reverse" ]; then
          rm -f skipstart
          rm -f geoPlusVel
          rm -f olddynrun
          rm -f olddynrun2
          rm -f olddynrun3
          a=`awk '{print $1}' isomernumber`
          mv traj traj$a
        fi
        if [ `cat skipstart` = "forward" ]; then
          echo reverserestart > skipstart
        fi
      else
        rm -f skipstart
        rm -f geoPlusVel
        rm -f olddynrun
        rm -f olddynrun2
        rm -f olddynrun3
        a=`awk '{print $1}' isomernumber`
        mv traj traj$a
      fi
      break
    fi
```

```
  done
#
END_of_C_Loop____END_of_C_Loop____END_of_C_Loop____END_of_C_Loop____END
_of_C_Loop____END_of_C_Loop____

# We've got to break a second time to get out of this loop
# if we really want to quit.  Otherwise, it will start over
# at the top
  if (test  -f nogo) then
    break
  fi
  if (test  -s $scratchdir/goingwell) then
    echo "starting a new point or a new direction"
  else
    break
  fi
done

  if (test  -f nogo) then
    break
  fi
  if (test  -s $scratchdir/goingwell) then
    echo "starting a new point or a new direction2"
  else
    break
  fi
done
exit 0
```

Program proggenHP

```
BEGIN {
# 2014 - avoids bug with a box on, so that starts without modes use input geometry, not standard orientation
# aug 2013 summary of changes
#includes molecular rotation, ability to do multiple NMR calculations, ONIOM with link atoms,
#nonstandard routes, handling of linear molecules using geometry linear, fixed but with atoms over 99 but
#bug varies with version of Gaussian, randomization based on PROCINFO (solved many problems), added initialDiss 3 for random
#phase of normal modes
# Aut 2010 changes classicalSpacing to 2 and upped possible excited states to 4000
# Jan 2009 - a number of little changes to improve reporting, precision, etc, specification of displacement on particular modes
# Jan 2009 cannonball trajectories.  adds desired energy to initial velocities based on file cannontraj, so one can shoot toward a ts
# updated Nov 2008 to incorporate running DRPs
# updated Nov 2008 to allow for start without an initial freq calc using classical = 2
```

```
# updated Aug 2008 added to atom list to handle a large number of atoms without changes needed
# updated June 2008 to incorportate new method for choosing displacements with initialdis 2
# updated Jan 17 2008 - bug fix for > 99 atoms, 300 excitations of low modes possible
# version August 2007 - incorporates classical trajectory calculation option
#also allows listing of number of imaginary frequencies
# version Sept 16, 2005 - incorportates searchdir but not yet rotation
# now reads random numbers from temp811, starting at a random place
# The input files are generated before this and are tempfreqs, tempredmass,
# tempfrc, tempmodes, and tempstangeos.
# It will count the number of atoms.

# default parameters, including quassiclassical, no displacements, transition state, not a DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
charge=0; multiplicity=1; method="HF/3-21G"; memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999
conver1=4.184E26 #dividing by this converts amu angs^2 /s^2 to kcal/mol
geometry="nonlinear";rotationmode=0

#initialization and constants
for (i=1;i<=10000;i++) {disMode[i]=-1}
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0; classicalSpacing=2
zpeGauss=0; zpeGaussK=0; zpePlusE=0; potentialE=0

# read progdyn.conf for configuration info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="initialdis") initialDis=$2
  if ($1=="timestep") timestep=$2
  if ($1=="scaling") scaling=$2
  if ($1=="temperature") temp=$2
  if ($1=="searchdir") searchdir=$2
  if ($1=="classical") classical=$2
```

```
  if ($1=="numimag") numimag=$2
  if ($1=="geometry") geometry=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="boxon") boxon=$2
  if ($1=="boxsize") boxsize=$2
  if ($1=="DRP") DRP=$2; if (DRP==1) classical=2 #this lets one start a DRP from a point
that is not a freq calc
  if ($1=="maxAtomMove") maxAtomMove=$2
  if ($1=="cannonball") cannonball=$2
  if ($1=="displacements") disMode[$2]=$3
  if ($1=="controlphase") controlPhase[$2]=$3
  if ($1=="rotationmode") rotationmode=$2
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
    }
  blankLineTester=length($0)
  }

if (diag>=1) print "***************** starting proggen *****************" >>
"diagnostics"
if (diag>=1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag>=1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag>=1) print "processors,checkpoint,title,initialdis,timestep,scaling,temperature" >>
"diagnostics"
if (diag>=1) print processors,checkpoint,title1,title2,title3,title4,initialDis,timestep,scaling,temp
>> "diagnostics"
if (diag>=1) print
"classical,numimag,highlevel,boxon,boxsize,DRP,maxAtomMove,cannonball" >>
"diagnostics"
if (diag>=1) print classical,numimag,highlevel,boxon,boxsize,DRP,maxAtomMove,cannonball
>> "diagnostics"

# put geometries into array, also figure out number of atoms
# note that this picks out the last geometry in a file, assuming
# that if there is an optimization followed by a freq, nothing else follows
# kludgy - repeats last line twice - must be a better way
do {
  getline < "tempstangeos"
  if (oldline==$0) $0=""
  oldline=$0
  atom = $1
  if (atom>numAtoms) numAtoms=atom
  atNum[atom]=$2
  geoArr[atom,1]=$4; geoArr[atom,2]=$5; geoArr[atom,3]=$6
  geoArrOrig[atom,1]=$4; geoArrOrig[atom,2]=$5; geoArrOrig[atom,3]=$6
```

```
  velArr[atom,1]=0; velArr[atom,2]=0; velArr[atom,3]=0
  }
while (length($0) > 0)

#output the number of atoms, used in many routines
print numAtoms

# put in atomic symbols and atomic weights - assigns a default mass but then reads it from tempmasses when possible
for (i=1;i<=numAtoms;i++) {
  getline < "tempmasses"
  if (atNum[i]==1) {atSym[i]="H";atWeight[i]=1.00783}
  if (atNum[i]==2) {atSym[i]="He";atWeight[i]=4.0026}
  if (atNum[i]==3) {atSym[i]="Li";atWeight[i]=6.941}
  if (atNum[i]==4) {atSym[i]="Be";atWeight[i]=9.012}
  if (atNum[i]==5) {atSym[i]="B";atWeight[i]=10.811}
  if (atNum[i]==6) {atSym[i]="C";atWeight[i]=12.}
  if (atNum[i]==7) {atSym[i]="N";atWeight[i]=14.007}
  if (atNum[i]==8) {atSym[i]="O";atWeight[i]=15.9994}
  if (atNum[i]==9) {atSym[i]="F";atWeight[i]=18.9984}
  if (atNum[i]==10) {atSym[i]="Ne";atWeight[i]=20.1797}
  if (atNum[i]==11) {atSym[i]="Na";atWeight[i]=22.989}
  if (atNum[i]==12) {atSym[i]="Mg";atWeight[i]=24.305}
  if (atNum[i]==13) {atSym[i]="Al";atWeight[i]=26.98154}
  if (atNum[i]==14) {atSym[i]="Si";atWeight[i]=28.0855}
  if (atNum[i]==15) {atSym[i]="P";atWeight[i]=30.9738}
  if (atNum[i]==16) {atSym[i]="S";atWeight[i]=32.066}
  if (atNum[i]==17) {atSym[i]="Cl";atWeight[i]=35.4527}
  if (atNum[i]==18) {atSym[i]="Ar";atWeight[i]=39.948}
  if (atNum[i]==19) {atSym[i]="K";atWeight[i]=39.0983}
  if (atNum[i]==20) {atSym[i]="Ca";atWeight[i]=40.078}
  if (atNum[i]==21) {atSym[i]="Sc";atWeight[i]=44.96}
  if (atNum[i]==22) {atSym[i]="Ti";atWeight[i]=47.867}
  if (atNum[i]==23) {atSym[i]="V";atWeight[i]=50.94}
  if (atNum[i]==24) {atSym[i]="Cr";atWeight[i]=51.9961}
  if (atNum[i]==25) {atSym[i]="Mn";atWeight[i]=54.938}
  if (atNum[i]==26) {atSym[i]="Fe";atWeight[i]=55.845}
  if (atNum[i]==27) {atSym[i]="Co";atWeight[i]=58.933}
  if (atNum[i]==28) {atSym[i]="Ni";atWeight[i]=58.693}
  if (atNum[i]==29) {atSym[i]="Cu";atWeight[i]=63.546}
  if (atNum[i]==30) {atSym[i]="Zn";atWeight[i]=65.38}
  if (atNum[i]==31) {atSym[i]="Ga";atWeight[i]=69.723}
  if (atNum[i]==32) {atSym[i]="Ge";atWeight[i]=72.64}
  if (atNum[i]==33) {atSym[i]="As";atWeight[i]=74.9216}
  if (atNum[i]==34) {atSym[i]="Se";atWeight[i]=78.96}
  if (atNum[i]==35) {atSym[i]="Br";atWeight[i]=79.904}
  if (atNum[i]==46) {atSym[i]="Pd";atWeight[i]=106.42}
  if (atNum[i]==53) {atSym[i]="I";atWeight[i]=126.90447}
```

```
# gets actual weight from freqinHP when possible so a prior calc with readisotopes gets you isotopic substitution
  if ((i<100) && ($9>0)) atWeight[i]=$9
#  if ((i>99) && ($8>0)) atWeight[i]=$8

  if ((diag>1) && (i==1)) print "atNum[i],atSym[i],atWeight[i],geoArr[i,1],geoArr[i,2],geoArr[i,3]" >> "diagnostics"
  if (diag>1) print atNum[i],atSym[i],atWeight[i],geoArr[i,1],geoArr[i,2],geoArr[i,3] >> "diagnostics"
  }

# read in frequencies, scale them, read in Reduced masses, read in force
#constants, replace negative frequencies by 2 wavenumbers
numFreq=3*numAtoms-6
if (geometry=="linear") numFreq=3*numAtoms-5
for (i=1;i<=numFreq;i++) {
  $0=""
  getline < "tempfreqs"
  freq[i]=$0*scaling
  if (freq[i]<0) freq[i]=2
  }
for (i=1;i<=numFreq;i++) {
  $0=""
  getline < "tempredmass"
  redMass[i]=$0
  if (redMass[i]=="") redMass[i]=1.
  }
for (i=1;i<=numFreq;i++) {
  $0=""
  getline < "tempfrc"
  frc[i]=$0
  if (frc[i]=="") frc[i]=0.0001
  if (frc[i]==0) frc[i]=0.0001
  if ((diag>1) && (i==1)) print "freq[i],redMass[i],frc[i]" >> "diagnostics"
  if (diag>1) print freq[i],redMass[i],frc[i] >> "diagnostics"
  }

# read in the modes - note that trajectories always need a freq calc with freq=hpmodes unless classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i+=5) {
    for (j=1;j<=(3*numAtoms);j++) {
      getline < "tempmodes"
      mode[i,$2,$1]=$4;  mode[i+1,$2,$1]=$5;  mode[i+2,$2,$1]=$6;  mode[i+3,$2,$1]=$7; mode[i+4,$2,$1]=$8
      }
    }
  }
```

```
if (diag>2) {for (i=1;i<=numFreq;i++) {print mode[i,1,1],mode[i,1,2],mode[i,1,3] >> "modesread"}}

# if doing a cannonball trajectory, read in the vector
if (cannonball>0) {
  for (i=1;i<=numAtoms;i++) {
    getline < "cannontraj"
    cannonArr[i,1]=$1; cannonArr[i,2]=$2; cannonArr[i,3]=$3
    }
  }

# collect a series of random numbers from file temp811, generated from an outside random number generator called by prodynstarterHP
# read from temp811, starting at a random place
srand(PROCINFO["pid"]); tester=rand()*1000
for (i=1;i<=tester;i++) getline < "temp811"
for (i=1;i<=numFreq;i++) {
  getline < "temp811"; randArr[i]=$1
  getline < "temp811"; randArrB[i]=$1
  getline < "temp811"; randArrC[i]=$1
}
if (rotationmode>0) {
  for (i=1;i<=6;i++) {
    getline < "temp811"; randArrR[i]=$1
  }
}

# for a QM distribution for a harmonic oscillator in its ground state, we want to generate a set of random numbers
#between -1 and 1 weighted such that numbers toward the center are properly more common
i=1
while (i<=numFreq) {
  if ((initialDis==2) || (disMode[i]==2)) {
    getline < "temp811"
    tempNum=2*($1-.5)
    prob=exp(-(tempNum^2))
    getline < "temp811"
    if ($1<prob) {
      randArrD[i]=tempNum
      i++
      }
    }
  if ((initialDis!=2) && (disMode[i]!=2)) i++
  }

# to start without normal modes or frequencies we need to just pick a random direction for the motion of each atom, requiring 3N random numbers
for (i=1;i<=numAtoms;i++) {
```

```
  for (j=1;j<=3;j++) {
  getline < "temp811"
  if ($1>0.5) randArrE[i,j]=1
  if ($1<.5) randArrE[i,j]=-1
    }
  }

# determine energy in each normal mode
for (i=1;i<=numFreq;i++) {
  zpeJ[i]=0.5*h*c*freq[i]      #units J per molecule
#if classical, treat as modes spaced by classicalSpacing wavenumbers
  if (classical==1) zpeJ[i]=0.5*h*c*classicalSpacing  # the zpe is not used when classical but
the spacing is used to calculate the E in mode
  zpeK[i]=zpeJ[i]*avNum/4184    #units kcal/mol
  if (temp<10) vibN[i]=0         # avoids working with very small temperatures - if the temp is
too low, it just acts like 0 K
  if (temp>=10) {
    zpeRat[i]=exp((-2*zpeK[i])/(RgasK*temp))
    if (zpeRat[i]==1) zpeRat[i]=.99999999999
    Q[i]=1/(1-zpeRat[i])
    newRand=randArr[i]
    vibN[i]=0
    tester=1/Q[i]
#    get up to 4000 excitations of low modes
    for (j=1;j<=(4000*zpeRat[i]+2);j++) {
      if (newRand>tester) vibN[i]++
      tester=tester+((zpeRat[i]^j)/Q[i])
      }
    }
  }

# figure out mode energies and maximum classical shift and then actual shift
# also calculated total energy desired for molecule
desiredModeEnK=0
for (i=1;i<=numFreq;i++) {
  modeEn[i]=(zpeJ[i]*1E18)*(2*vibN[i]+1)  # units here are mDyne Ansgroms for
compatability with Gaussian force constants
  if (classical==1) modeEn[i]=(zpeJ[i]*1E18)*2*vibN[i]    #no zpe when classical
  modeEnK[i]=zpeK[i]*(2*vibN[i]+1)
  if (classical==1) modeEnK[i]=zpeK[i]*2*vibN[i]         #no zpe when classical
  desiredModeEnK=desiredModeEnK + modeEnK[i]
# no 1/2 hv for imaginary frequencies
# treating modes with frequencies <10 as translations, ignoring their zero point energies
  if (freq[i]<10) modeEn[i]=(zpeJ[i]*1E18)*(2*vibN[i])
  maxShift[i]=(2*modeEn[i]/frc[i])^0.5
# new 2012 initialDis 3 means random phase of normal mode
  if (initialDis==3) shift[i]=maxShift[i]*sin(randArrC[i]*3.141592*2)
  if (initialDis==2) shift[i]=maxShift[i]*randArrD[i]
```

```
  if (initialDis==1) shift[i]=maxShift[i]*(2*(randArrC[i]-0.5))
  if (initialDis==0) shift[i]=0
# lines below allow for setting of displacement mode for individual modes
# It used to be necessary to use disMode 10 to turn off displacements for a mode, but hopefully
that bug is killed and you can use disMode 0
  if (disMode[i]==3) shift[i]=maxShift[i]*sin(randArrC[i]*3.141592*2)
  if (disMode[i]==2) shift[i]=maxShift[i]*randArrD[i]
  if (disMode[i]==1) shift[i]=maxShift[i]*(2*(randArrC[i]-0.5))
  if (disMode[i]==10) shift[i]=0 #kept for backward compatability
  if (disMode[i]==0) shift[i]=0
# no displacements along imaginary frequencies and very low ones - it is better to treat these
# as translations - employing a shift can give you initial weird geometries
  if (freq[i]<10) shift[i]=0
  if (numimag==1) shift[1]=0
  if (numimag==2) shift[2]=0
  }
for (i=1;i<=numFreq;i++) {
  if ((diag>1) && (i==1)) print
"zpeJ[i],zpeK[i],zpeRat[i],Q[i],vibN[i],modeEn[i],maxShift[i],shift[i]" >> "diagnostics"
  if (diag>1) print zpeJ[i],zpeK[i],zpeRat[i],Q[i],vibN[i],modeEn[i],maxShift[i],shift[i] >>
"diagnostics"
  }

# multiply each of the modes by its shift and add them up
# Do not do this if classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i++) {
    for (j=1;j<=numAtoms;j++) {
      for (k=1;k<=3;k++) {
        shiftMode[i,j,k]=mode[i,j,k]*shift[i]
        geoArr[j,k]=geoArr[j,k]+shiftMode[i,j,k]
        }
      }
    }
  }

#now start toward velocities
for (i=1;i<=numFreq;i++) {
  kinEn[i]=100000*(modeEn[i]-0.5*frc[i]*shift[i]^2)  # the 100000 converts to g angstrom^2
s^2
  vel[i]=(2*kinEn[i]/(redMass[i]/avNum))^0.5       # in angstrom / s
#use searchdir in progdyn.conf to control the direction for trajectories started from a saddle
point
  if (numimag>1) numimag=1  #only the first freq can be sent in the searchdir direction, the
rest go in a random direction
  if (i>numimag) {
    if (randArrB[i]<0.5) vel[i]=-vel[i]
    }
```

```
  if (i==numimag) {
    if (searchdir=="negative") vel[i]=-vel[i]
    }
  if ((diag>1) && (i==1)) print "vel[i]" >> "diagnostics"
  if (diag>1) print vel[i] >> "diagnostics"
  }

# if controlphase is being used, set the velocity on particular modes as positive or negative as
requested
for (i=1;i<=numFreq;i++) {
  if ((controlPhase[i]=="positive") && (vel[i]<0)) vel[i]=-vel[i]
  if ((controlPhase[i]=="negative") && (vel[i]>0)) vel[i]=-vel[i]
  }

# multiply each of the modes by its velocity and add them up
# Do not do this if classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i++) {
    for (j=1;j<=numAtoms;j++) {
      for (k=1;k<=3;k++) {
        velMode[i,j,k]=mode[i,j,k]*vel[i]*timestep
        velArr[j,k]=velArr[j,k]+velMode[i,j,k]
        }
      }
    }
  }

# to start without normal modes or frequencies we figure out the energy per atom based on
1/2RT in degree of freedom
if (classical==2) {
# to avoid a bug with a box on, starts without modes should use the input geometry, not the
standard
  do {
    getline < "tempinputgeos"
    if (oldline==$0) $0=""
    oldline=$0
    atom = $1
    geoArr[atom,1]=$4; geoArr[atom,2]=$5; geoArr[atom,3]=$6
    geoArrOrig[atom,1]=$4; geoArrOrig[atom,2]=$5; geoArrOrig[atom,3]=$6
    }
  while (length($0) > 0)
  degFreedomEnK=temp*RgasK
  degFreedomEnJ=degFreedomEnK/(avNum/4184)
  cartEn=degFreedomEnJ*1E18
  kinEnCart=100000*cartEn
#print degFreedomEnK, degFreedomEnJ, cartEn, kinEnCart
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
```

```
      velArr[i,j]=randArrE[i,j]*timestep*(2*kinEnCart/(atWeight[i]/avNum))^0.5
      if (DRP==1) velArr[i,j]=0
      }
    }
  }

# calculate the KE in the modes at this point
KEinitmodes=0
for (j=1;j<=numAtoms;j++) {
  KEinitmodes=KEinitmodes + 0.5*atWeight[j]*(velArr[j,1]^2 + velArr[j,2]^2 +
velArr[j,3]^2)/((timestep^2)*conver1)
  }

# add molecular rotation if requested
if (rotationmode>0) {
#establish three rotation vectors
  for (j=1;j<=numAtoms;j++) {
    rotateX[j,1]=0
    rotateX[j,2]=-geoArrOrig[j,3]
    rotateX[j,3]=geoArrOrig[j,2]
    rotateY[j,1]=-geoArrOrig[j,3]
    rotateY[j,2]=0
    rotateY[j,3]=geoArrOrig[j,1]
    rotateZ[j,1]=-geoArrOrig[j,2]
    rotateZ[j,2]=geoArrOrig[j,1]
    rotateZ[j,3]=0
    }
#figure out how much energy is in the raw vectors
  eRotX=0;eRotY=0;eRotZ=0
  for (j=1;j<=numAtoms;j++) {
    for (k=1;k<=3;k++) {
      eRotX=eRotX + 0.5*atWeight[j]*(rotateX[j,k]^2)/((timestep^2)*conver1)
      eRotY=eRotY + 0.5*atWeight[j]*(rotateY[j,k]^2)/((timestep^2)*conver1)
      eRotZ=eRotZ + 0.5*atWeight[j]*(rotateZ[j,k]^2)/((timestep^2)*conver1)
      }
    }
#  print "rotation energies if raw vector used",eRotX,eRotY,eRotZ
#now deciie how much energy we want in each rotation
  keRx=-0.5*0.001987*temp*log(1-randArrR[1])
  keRy=-0.5*0.001987*temp*log(1-randArrR[2])
  keRz=-0.5*0.001987*temp*log(1-randArrR[3])
  if (eRotX<1) keRx=0;if (eRotY<1) keRy=0;if (eRotZ<1) keRz=0
  rotEdesired=keRx+keRy+keRz
  signX=1;signY=1;signZ=1
  if (randArrR[4]<.5) signX=-1
  if (randArrR[5]<.5) signY=-1
  if (randArrR[6]<.5) signZ=-1
```

```
#                print "desired energies",keRx,keRy,keRz,"and random
numbers",randArrR[1],randArrR[2],randArrR[3]
#protect against zero rotations
  if (eRotX<1) eRotX=1;if (eRotY<1) eRotY=1;if (eRotZ<1) eRotZ=1
#now scale the rotational vectors
  scaleX=(keRx/eRotX)^.5
  scaleY=(keRy/eRotY)^.5
  scaleZ=(keRz/eRotZ)^.5
#  print "scaling factors" scaleX,scaleY,scaleZ
  for (j=1;j<=numAtoms;j++) {
    for (k=1;k<=3;k++) {
      rotateX[j,k]=rotateX[j,k]*scaleX*signX
      rotateY[j,k]=rotateY[j,k]*scaleY*signY
      rotateZ[j,k]=rotateZ[j,k]*scaleZ*signZ
      }
    }
  for (j=1;j<=numAtoms;j++) {
#    print rotateX[j,1],"   ",rotateX[j,2],"   ",rotateX[j,3]
    }
#  print ""
  for (j=1;j<=numAtoms;j++) {
#    print rotateY[j,1],"   ",rotateY[j,2],"   ",rotateY[j,3]
    }
#  print ""
  for (j=1;j<=numAtoms;j++) {
#    print rotateZ[j,1],"   ",rotateZ[j,2],"   ",rotateZ[j,3]
    }
# now add the rotational vectors  to velArr
  for (j=1;j<=numAtoms;j++) {
    for (k=1;k<=3;k++) {
      velArr[j,k]=velArr[j,k]+rotateX[j,k]+rotateY[j,k]+rotateZ[j,k]
      }
    }
  }

# if doing a cannonball, adjust multiplier until extra energy is correct
if (cannonball>0) {
  multiplier=1; tester=0; tolerance=.1
  while (tester==0) {
    KEinittotal=0
    for (j=1;j<=numAtoms;j++) {
      cannonvelArr[j,1]=velArr[j,1]+multiplier*cannonArr[j,1];
cannonvelArr[j,2]=velArr[j,2]+multiplier*cannonArr[j,2];
cannonvelArr[j,3]=velArr[j,3]+multiplier*cannonArr[j,3]
      KEinittotal=KEinittotal + 0.5*atWeight[j]*(cannonvelArr[j,1]^2 + cannonvelArr[j,2]^2 +
cannonvelArr[j,3]^2)/((timestep^2)*conver1)
      }
    if (KEinittotal>(KEinitmodes+cannonball+tolerance)) multiplier=multiplier*0.98901364
```

```
    if (KEinittotal<(KEinitmodes+cannonball-tolerance)) multiplier=multiplier*1.01
    if ((KEinittotal<(KEinitmodes+cannonball+tolerance)) &&
(KEinittotal>(KEinitmodes+cannonball-tolerance))) tester=1
    }
  for (j=1;j<=numAtoms;j++) {
    velArr[j,1]=velArr[j,1]+multiplier*cannonArr[j,1];
velArr[j,2]=velArr[j,2]+multiplier*cannonArr[j,2];
velArr[j,3]=velArr[j,3]+multiplier*cannonArr[j,3]
    }
  }

#output the new geometry.
# ****** this section changed for special experiment for cyclopentadiene.  do not use this for
other cases
# atWeight[4]=140.0001
# ****** line below added for special experiment switching mass from 12 to 140, keeping
momenta the same
#velArr[4,1]=velArr[4,1]/11.66667;                    velArr[4,2]=velArr[4,2]/11.66667;
velArr[4,3]=velArr[4,3]/11.66667
for (j=1;j<=numAtoms;j++) {
  printf("%2s % .7f % .7f % .7f %9.5f
\n",atSym[j],geoArr[j,1],geoArr[j,2],geoArr[j,3],atWeight[j])
  }

#output the velocities and calculate the total kinetic energy overall
KEinittotal=0
for (j=1;j<=numAtoms;j++) {
  KEinittotal=KEinittotal + 0.5*atWeight[j]*(velArr[j,1]^2 + velArr[j,2]^2 +
velArr[j,3]^2)/((timestep^2)*conver1)
  printf("% .8f % .8f % .8f \n",velArr[j,1],velArr[j,2],velArr[j,3])
  }

#anything else I add to the file will not affect the trajectories but will keep a record and be
good for analysis
if (classical!=2) {
  for (i=1;i<=numFreq;i++) {
    if (initialDis==0) printf("%.6f % .6f %4i % 1.4e % .6f %1i\n", randArr[i],
randArrB[i], vibN[i], vel[i], shift[i], disMode[i])
    if (initialDis==1) printf("%.6f % .6f %4i % 1.4e % .6f %1i\n", randArr[i],
randArrC[i], vibN[i], vel[i], shift[i], disMode[i])
    if (initialDis==2) printf("%.6f % .6f %4i % 1.4e % .6f %1i\n", randArr[i],
randArrD[i], vibN[i], vel[i], shift[i], disMode[i])
    if (initialDis==3) printf("%.6f % .6f %4i % 1.4e % .6f %1i % .6f\n", randArr[i],
randArrC[i], vibN[i], vel[i], shift[i], disMode[i], sin(randArrC[i]*3.141592*2))
    }
  }
print "temp ",temp
print "initialDis",initialDis
```

```
print "classical",classical
print "timestep",timestep
print "numimag",numimag
OFMT = "%.3f"
print "Total mode energy desired=",desiredModeEnK
print "KE initial from modes=",KEinitmodes,"    KE initial total=",KEinittotal,"    Rotational
Energy desired=",rotEdesired
if (cannonball>0) print "cannonball",cannonball,"  cannon Energy=",KEinittotal-KEinitmodes
if (boxon>0) print "boxsize",boxsize
if (DRP>0) print "DRP",DRP,"   maxAtomMove",maxAtomMove
if (DRP>0) print maxAtomMove > "maxMove"
}  # End of BEGIN

/Zero-point correction/ {zpeGauss=$3}
/zero-point Energies/ {zpePlusE=$7}
END {
zpeGaussK=zpeGauss*627.509
potentialE=zpePlusE - zpeGauss
OFMT = "%.6f"
print "Gaussian zpe=",zpeGauss,"or",zpeGaussK,"kcal/mol   E + zpe=",zpePlusE,"   potential
E=",potentialE
print "" #will use blank line to mark end of geoPlusVel file
}
```

Program prog1stpoint

```
BEGIN {
# 2014 added ONIOMcharge, more reliable convergence commands
# 2013 added multiple NMR calculations, molecular rotations
# 2012 added NMR calculations
# 2011 added linkatoms in ONIOM
# aug 2010 changed so that it is more careful in reading in from geoPlusVel
#     removed some default parameters that should always be defined
# Jan 2009 - a number of little changes to improve reporting, precision, etc
# aug 2008 added to atom list so handles H to Cl without change needed
# version Feb 2008 incorporates methodfile, boxon and boxsize, though this point unaffected by
box
# version Jan 2008 - allows for ONIOM jobs, fixed atoms
# version Sept 2005 - incorportates meth3, meth4, meth5, meth6, but not yet rotation
# this program creates the first input file for g09
# the title should be changed as appropriate
# the isomer number comes from a file isomernumber

# default parameters, including quassiclassical, no displacements, transition state, not a DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
```

```
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999; linkatoms=0
geometry="nonlinear";nonstandard=0
nmrtype=0;nmrevery=9999999
oniomcharge=0; oniommult=0

#initialization
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0
getline < "runpointnumber"
runpointnum = $1

# read progdyn.conf for configuration info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="method2") meth2=$2
  if ($1=="charge") charge=$2
  if ($1=="oniomchargemult") {
    oniomcharge=$2
    oniommult=$3
    }
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="timestep") timestep=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="method3") meth3=$2
  if ($1=="method4") meth4=$2
  if ($1=="method5") meth5=$2
  if ($1=="method6") meth6=$2
  if ($1=="method7") meth7=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="linkatoms") linkatoms=$2
  if ($1=="fixedatom1") fixedatom1=$2
  if ($1=="fixedatom2") fixedatom2=$2
  if ($1=="fixedatom3") fixedatom3=$2
  if ($1=="fixedatom4") fixedatom4=$2
  if ($1=="methodfile") methodfilelines=$2
  if ($1=="killcheck") killcheck=$2
  if ($1=="NMRmethod") nmrmethod=$2
  if ($1=="NMRmethod2") nmrmethod2=$2
  if ($1=="NMRmethod3") nmrmethod3=$2
  if ($1=="NMRtype") nmrtype=$2
```

```
  if ($1=="NMRevery") nmrevery=$2
  if ($1=="nonstandard") nonstandard=$2
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
    }
  blankLineTester=length($0)
  }

if (diag==1) print "***************** starting prog1stpoint *****************" >>
"diagnostics"
if (diag==1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag==1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag==1) print "processors,checkpoint,title" >> "diagnostics"
if (diag==1) print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"

getline < "isomernumber"
isomernum = $1
#read in number of atoms, geometry, masses, and velocity from geoPlusVel
getline < "geoPlusVel"
numAtoms=$1
# geometry
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  weight[i]=$5
  atSym[i]=$1
  for (j=1;j<=3;j++) {
    geoArr[i,j]=$(1+j)
    }
  }
#velocities not needed for 1st point
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  for (j=1;j<=3;j++) {
    velArr[i,j]=$j
    }
  }

print "%nproc=" processors
print "%mem=" memory
if (killcheck!=1) print "%chk=" checkpoint
if (nonstandard==0) {
  print "# " method " force scf=(xqc,maxconven=55,fulllinear,nosym) "
  if (meth2=="unrestricted") print "guess=mix" #for unrestricted calculations
  if (length(meth3)>2) print meth3
  if (length(meth4)>2) print meth4
```

```
  }
if (nonstandard==1) {
  print "# "
  print "nonstd"
  system("cat nonstandard")
  }
print ""
# make the title four words exactly, leaving out spaces if necessary
print title1,title2,title3,title4
print "runpoint ",runpointnum
print "runisomer ", isomernum
print ""
if (oniommult==0) print charge,multiplicity
if (oniommult>0) print charge,multiplicity,oniomcharge,oniommult
}

END {
for (i=1;i<=numAtoms;i++) {
  printf("%s %.7f %.7f %.7f",atSym[i],geoArr[i,1],geoArr[i,2],geoArr[i,3])
  if ((i>highlevel) && (i<=highlevel+linkatoms)) printf(" %s","M H")
  if (i>(highlevel+linkatoms)) printf(" %s","M")
  print ""
  }
print ""
if (length(meth5)>2) print meth5
if (length(meth6)>2) print meth6
if (methodfilelines>=1) {
  for (i=1;i<=methodfilelines;i++) {
    getline < "methodfile"
    print $0
    }
  }
if ((nmrtype>0) && ((runpointnum % nmrevery)==0)) {
  print "--link1--"
  print "%nproc=" processors
  print "%mem=" memory
  print "%chk=" checkpoint
  print "# " nmrmethod " nmr=giao geom=check"
  if (nmrmethod==method) print "guess=tcheck"
  if (length(meth7)>2) print meth7
  print ""
  print title1,title2,title3,title4
  print "runpoint ",runpointnum
  print "runisomer ",isomernum
  print ""
  print charge,multiplicity
  }
print ""
```

```
if ((nmrtype>1) && ((runpointnum % nmrevery)==0)) {
  print "--link1--"
  print "%nproc=" processors
  print "%mem=" memory
  print "%chk=" checkpoint
  print "# " nmrmethod2 " nmr=giao geom=check"
  if (length(meth7)>2) print meth7
  print ""
  print title1,title2,title3,title4
  print "runpoint ",runpointnum
  print "runisomer ",isomernum
  print ""
  print charge,multiplicity
  }
print ""
if ((nmrtype>2) && ((runpointnum % nmrevery)==0)) {
  print "--link1--"
  print "%nproc=" processors
  print "%mem=" memory
  print "%chk=" checkpoint
  print "# " nmrmethod3 " nmr=giao geom=check"
  if (length(meth7)>2) print meth7
  print ""
  print title1,title2,title3,title4
  print "runpoint ",runpointnum
  print "runisomer ",isomernum
  print ""
  print charge,multiplicity
  }
print ""
}
```

Program prog2ndpoint

```
BEGIN {
# 2014 added ONIOMcharge, more reliable convergence commands
# aug 2013 includes molecular rotation, ability to do multiple NMR calculations, ONIOM with link atoms,
#nonstandard routes, checks more kinds of energies at point 2
#Aug 2010 added etolerance to make it controllable from progdyn.conf, made it so that DRP does not check energy
# aug 2008 added to atom list so handles 1 to 17 without change needed
# version Feb 2008 incorporates methodfile, boxon and boxsize, though this point unaffected by box
# version Jan 2008 - allows for ONIOM jobs, fixed atoms
# version Sept 9, 2005 - incorportates meth3, meth4, meth5, meth6, but not yet rotation
# read progdyn.conf for configuration info

# default parameters, including quassiclassical, no displacements, transition state, not a DRP
```

```
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999; linkatoms=0
etolerance=1
geometry="nonlinear";nonstandard=0
NMRtype=none;NMRevery=9999999
oniomcharge=0; oniommult=0

#initialization
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0
getline < "runpointnumber"
runpointnum = $1

blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="method2") meth2=$2
  if ($1=="charge") charge=$2
  if ($1=="oniomchargemult") {
    oniomcharge=$2
    oniommult=$3
    }
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="timestep") timestep=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="method3") meth3=$2
  if ($1=="method4") meth4=$2
  if ($1=="method5") meth5=$2
  if ($1=="method6") meth6=$2
  if ($1=="method7") meth7=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="linkatoms") linkatoms=$2
  if ($1=="fixedatom1") fixedatom1=$2
  if ($1=="fixedatom2") fixedatom2=$2
  if ($1=="fixedatom3") fixedatom3=$2
  if ($1=="fixedatom4") fixedatom4=$2
  if ($1=="DRP") DRP=$2
```

```
  if ($1=="methodfile") methodfilelines=$2
  if ($1=="killcheck") killcheck=$2
  if ($1=="etolerance") etolerance=$2
  if ($1=="reversetraj") reversetraj=$2
  if ($1=="NMRmethod") nmrmethod=$2
  if ($1=="NMRmethod2") nmrmethod2=$2
  if ($1=="NMRmethod3") nmrmethod3=$2
  if ($1=="NMRtype") nmrtype=$2
  if ($1=="NMRevery") nmrevery=$2
  if ($1=="nonstandard") nonstandard=$2
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
    }
  blankLineTester=length($0)
  }

if (diag>=1) print "***************** starting prog2ndpoint ****************" >>
"diagnostics"
if (diag>=1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag>=1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag>=1) print "processors,checkpoint,title" >> "diagnostics"
if (diag>=1) print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"

#get the isomer number from file
getline < "isomernumber"
isomernum = $1

#get forward or reverse from skipstart if it exists
getline < "skipstart"
trajdirection = $1

print "%nproc=" processors
print "%mem=" memory
if (killcheck!=1) print "%chk=" checkpoint
if (nonstandard==0) {
  print "# " method " force scf=(xqc,maxconven=55,fulllinear,nosym) "
  if (meth2=="unrestricted") print "guess=mix" #for unrestricted calculations
  if (meth2=="read") print "guess=tcheck" #for reading orbitals from check, sometimes faster,
sometimes not
  if (length(meth3)>2) print meth3
  if (length(meth4)>2) print meth4
  }
if (nonstandard==1) {
  print "# "
  print "nonstd"
```

```
  system("cat nonstandard")
  }
print ""
print title1,title2,title3,title4
print "runpoint ",runpointnum
print "runisomer ", isomernum
print ""
if (oniommult==0) print charge,multiplicity
if (oniommult>0) print charge,multiplicity,oniomcharge,oniommult

# ok, now we have to figure the second point.  this should be
# x(t) = x + v*t + 1/2*F*t^2/m
# so we need to set up arrays for position, velocity, and force

#read in number of atoms, geometry, masses, and velocity from geoPlusVel
getline < "geoPlusVel"
numAtoms=$1
# geometry
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  weight[i]=$5
  atSym[i]=$1
  for (j=1;j<=3;j++) {
    geoArr[i,j]=$(1+j)
    }
  }
#velocities
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  for (j=1;j<=3;j++) {
    velArr[i,j]=$j
    }
  }

#now we go ahead and add the velocities
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
    arr[i,j]=velArr[i,j]+geoArr[i,j]
    if (trajdirection=="reverserestart") arr[i,j]=geoArr[i,j]-velArr[i,j]
    }
  if ((diag>1) && (i==1)) print "geometry after adding velocities" >> "diagnostics"
  if (diag>1) print arr[i,1],arr[i,2],arr[i,3] >> "diagnostics"
  }

#pull out other information useful for testing whether total energy is right or bad
blankLineTester=10
while (blankLineTester>1) {
  getline < "geoPlusVel"
```

```
  if ($4=="desired=") desiredModeEnK=$5
  if ($4=="modes=") {
    KEinitmodes=$5
    KEinittotal=$9
    }
  if ($11=="potential") potentialE=$13
  blankLineTester=length($0)
  }
#get initial geometry into file traj
print numAtoms >> "traj"
print potentialE,title1,title2,title3,title4,"runpoint 1 ","runisomer ",isomernum >> "traj"
for (i=1;i<=numAtoms;i++) {
  print atSym[i],geoArr[i,1],geoArr[i,2],geoArr[i,3] >> "traj"
  }
#added by Samae on 102910
scfcount=0
} # end of BEGIN

#pull out the potential energy
/SCF Done/ || /EUMP2 =/ || / Energy=/ {
if (($1=="Energy=") && ($3=="NIter="))  newPotentialE=$2
if (($1=="SCF") && (scfcount==0)) newPotentialE=$5
if ($1=="E2") {
  tempstring=$6
  split(tempstring, arr10, "D")
  newPotentialE=arr10[1]*(10^arr10[2])
  }
newPotentialEK=(newPotentialE-potentialE)*627.509
if ($1=="SCF") {
  if (scfcount==0) {
    pddga=$5
    }
  if (scfcount==1) {
    qm=$5
    }
  if (scfcount==2) {
    pddgb=$5
    pddgc=(pddga-pddgb)
    newPotentialE=(qm+pddgc)
    newPotentialEK=(newPotentialE-potentialE)*627.509
    }
  scfcount++
  }
}

# now we go ahead and translate the forces and add them
(/      1    / || /      2    / || /      3    / || /      4    / || /      5    / || /      6    / || /      7    / || /      8
/ || /      9    / || /      10    / || /      11    / || /      12    / || /      13    / || /      14    / || /      15    / || /
```

```
16    / || /      17    / || /      18    / || /      19    / || /      20    / || /      21    / || /      22    / || /      23    /
|| /      24    / || /      25    / || /      26    / || /      27    / || /      28    / || /      29    / || /      30    / || /
31    / || /      32    / || /      33    / || /      34    / || /      35    /) && length($3) > 9 {
i=$1
for (j=1;j<=3;j++) {
  forceArr[i,j]=$(2+j)    #the raw units of the forces are Hartree/Bohr
  }
if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
"diagnostics"
if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
}

END {
#put out Echeck but only if not a DRP
if (DRP==0) {
  print "trajectory #",isomernum >> "Echeck"
  print "point 1 potential E=",newPotentialEK,"      point 1 kinetic E=",KEinitmodes,"
Total=",newPotentialEK+KEinitmodes >> "Echeck"
  print "desired total energy=", desiredModeEnK >> "Echeck"
  if ((newPotentialEK+KEinitmodes)>(desiredModeEnK+etolerance)) print "XXXX bad total
Energy" >> "Echeck"
  if ((newPotentialEK+KEinitmodes)<(desiredModeEnK-etolerance)) print "XXXX bad total
Energy" >> "Echeck"
  }
# turn the forces into motion
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then mult time
(s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=0.5*1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/(weight
[i]/(avNum*1000))
# for simplicity, DRPs will throw away the forces at the second pont.  This means that if we are
not at a saddlepoint, point 2 = point 1 but this is a minor waste
    if (DRP==1) forceArr[i,j]=0
    arr[i,j]=arr[i,j]+forceArr[i,j]
# if atoms are fixed, replace calcd new position by original position
    if ((i==fixedatom1) || (i==fixedatom2) || (i==fixedatom3) || (i==fixedatom4))
arr[i,j]=geoArr[i,j]
    }
  if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
"diagnostics"
  if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
  printf("%s %.7f %.7f %.7f",atSym[i],arr[i,1],arr[i,2],arr[i,3])
  if ((i>highlevel) && (i<=highlevel+linkatoms)) printf(" %s","M H")
  if (i>(highlevel+linkatoms)) printf(" %s","M")
  print ""
  }
```

```
print ""
if (length(meth5)>2) print meth5
if (length(meth6)>2) print meth6
if (methodfilelines>=1) {
  for (i=1;i<=methodfilelines;i++) {
    getline < "methodfile"
    print $0
    }
  }
if ((nmrtype>0) && ((runpointnum % nmrevery)==0)) {
  print "--link1--"
  print "%nproc=" processors
  print "%mem=" memory
  print "%chk=" checkpoint
  print "# " nmrmethod " nmr=giao geom=check"
  if (nmrmethod==method) print "guess=tcheck"
  if (length(meth7)>2) print meth7
  print ""
  print title1,title2,title3,title4
  print "runpoint ",runpointnum
  print "runisomer ",isomernum
  print ""
  print charge,multiplicity
  }
print ""
if ((nmrtype>1) && ((runpointnum % nmrevery)==0)) {
  print "--link1--"
  print "%nproc=" processors
  print "%mem=" memory
  print "%chk=" checkpoint
  print "# " nmrmethod2 " nmr=giao geom=check"
  if (length(meth7)>2) print meth7
  print ""
  print title1,title2,title3,title4
  print "runpoint ",runpointnum
  print "runisomer ",isomernum
  print ""
  print charge,multiplicity
  }
print ""
if ((nmrtype>2) && ((runpointnum % nmrevery)==0)) {
  print "--link1--"
  print "%nproc=" processors
  print "%mem=" memory
  print "%chk=" checkpoint
  print "# " nmrmethod3 " nmr=giao geom=check"
  if (length(meth7)>2) print meth7
  print ""
```

```
  print title1,title2,title3,title4
  print "runpoint ",runpointnum
  print "runisomer ",isomernum
  print ""
  print charge,multiplicity
  }
print ""
#get second geometry into file traj
print numAtoms >> "traj"
print newPotentialE,title1,title2,title3,title4,"runpoint ",runpointnum,"runisomer ",isomernum >>
"traj"
for (i=1;i<=numAtoms;i++) {
  print atSym[i],arr[i,1],arr[i,2],arr[i,3] >> "traj"
  }
}
```

Program progdynb

```
BEGIN { #this is the main routine for generating new .com files by the Verlet algorithym
# Oct 2015 added sanity check, elimiated dyn files and keepevery
# May 2015 added ability to force solvent into a sphere
# Feb 2015 added zeroatom ability to make solute centered in solvent
# Jan 2015 added applyforce to apply forces on motion of atoms and allow PMF calculations
# Dec 2014 added oniom charge specifications
# 2013 added multiple NMR calculations, molecular rotations, thermostat commands
# 2012 added NMR calculations
# 2011 added linkatoms in ONIOM
# Aug 2010 increased elements handled automatically but only up to bromine!
# Jan 2009 - a number of little changes to improve reporting, precision, etc
# Nov 2008 added ability to handle DRPs
# Aug 2008 added long list of atoms to handle 1-17 without change
# May 2008 added option to put out velocities in vellist - make diag=3
# version Feb 2008 incorporates methodfile, boxon and boxsize
# version Jan 2008 incorporates fixed atoms, oniom, and velocity damping
# version August 2007 incorporates keepevery to decrease size of dyn file
# version Sept 11, 2005 - incorportates meth3, meth4, meth5, meth6, but not yet rotation

# default parameters, including quassiclassical, no displacements, transition state, not a DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=99999; linkatoms=0
damping=1;nonstandard=0
nmrtype=0;nmrevery=9999999;nmrcc=0;nmrrand=0;nmrdo=0
thermostat=0;thermostatemult=1.00
oniomcharge=0; oniommult=0
```

```
applyforce=0; applyforceB=0; applyforceC=0; zeroatomon=0
sphereon=0; spheresize=999; sphereforceK=0.01

#initialization
srand(PROCINFO["pid"])
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447; pi=3.14159265359
numAtoms=0; atomnumber=0
conver1=4.184E26 #dividing by this converts amu angs^2 /s^2 to kcal/mol
OFS="   "

# read progdyn.conf for configuration info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="method2") meth2=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="oniomchargemult") {
    oniomcharge=$2
    oniommult=$3
    }
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="timestep") timestep=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="temperature") temp=$2
  if ($1=="thermostat") thermostat=$2
  if ($1=="thermostatmult") thermostatmult=$2
  if (thermostatmult>1) thermostatmult=1/thermostatmult
  if ($1=="method3") meth3=$2
  if ($1=="method4") meth4=$2
  if ($1=="method5") meth5=$2
  if ($1=="method6") meth6=$2
  if ($1=="method7") meth7=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="linkatoms") linkatoms=$2
  if ($1=="fixedatom1") fixedatom1=$2
  if ($1=="fixedatom2") fixedatom2=$2
  if ($1=="fixedatom3") fixedatom3=$2
  if ($1=="fixedatom4") fixedatom4=$2
  if ($1=="boxon") boxon=$2
  if ($1=="boxsize") boxsize=$2
  if ($1=="sphereon") sphereon=$2
  if ($1=="spheresize") spheresize=$2
```

```
if ($1=="sphereforce") sphereforceK=$2
if ($1=="DRP") DRP=$2
if ($1=="maxAtomMove") maxAtomMove=$2
if ($1=="methodfile") methodfilelines=$2
if ($1=="killcheck") killcheck=$2
if ($1=="damping") damping=$2
if ($1=="NMRmethod") nmrmethod=$2
if ($1=="NMRmethod2") nmrmethod2=$2
if ($1=="NMRmethod3") nmrmethod3=$2
if ($1=="NMRtype") nmrtype=$2
if ($1=="NMRevery") nmrevery=$2
if ($1=="NMRrand") nmrrand=$2
if ($1=="loadlimit") loadlimit=$2
if ($1=="NMRcc") nmrcc=$2
if ($1=="nonstandard") nonstandard=$2
if ($1=="applyforce") {
  applyforce=$2; apforce=$3; apforceX0=$4; apforce2=$5; apforce3=$6
  }
if ($1=="applyforceB") {
  applyforceB=$2; apforceB=$3; apforceX0B=$4; apforce2B=$5; apforce3B=$6
  }
if ($1=="applyforceC") {
  applyforceC=$2; apforceC=$3; apforceX0C=$4; apforce2C=$5; apforce3C=$6
  }
if ($1=="afatoms") {
  for (i=1;i<8;i++) {
    if ($(i+1)>0) afatom[i]=$(i+1)
    }
  }
if ($1=="afatomsB") {
  for (i=1;i<8;i++) {
    if ($(i+1)>0) afatomB[i]=$(i+1)
    }
  }
if ($1=="afatomsC") {
  for (i=1;i<8;i++) {
    if ($(i+1)>0) afatomC[i]=$(i+1)
    }
  }
if ($1=="zeroatom") {
  zeroatomon=1
  zeroatom=$2
  }
if ($1=="title") {
  title1=$2
  title2=$3
  title3=$4
  title4=$5
```

```
    }
  blankLineTester=length($0)
  }

if (diag>=1) print "***************** starting progdynb *****************" >>
"diagnostics"
if (diag>=1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag>=1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag>=1) print "processors,checkpoint,title" >> "diagnostics"
if (diag>=1) print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"

# get number of atoms and weights from geoPlusVel, and previous geometries from old and
older
getline < "geoPlusVel"
numAtoms=$1
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  weight[i]=$5; atSym[i]=$1
  }
blankLineTester=10
while (blankLineTester>1) {
  getline < "geoPlusVel"
  if ($11=="potential") potentialE=$13
  blankLineTester=length($0)
  }

for (at=1;at<=numAtoms;at++) {
  getline < "old"
  oldarr[at,1]=$4; oldarr[at,2]=$5; oldarr[at,3]=$6
  }

for (at=1;at<=numAtoms;at++) {
  getline < "older"
  olderarr[at,1]=$4; olderarr[at,2]=$5; olderarr[at,3]=$6
  }

#for DRPs read in oldAdjForces and maxAtomMove
if (DRP==1) {
  for (at=1;at<=numAtoms;at++) {
    getline < "oldAdjForces"
    oldForce[at,1]=$1; oldForce[at,2]=$2; oldForce[at,3]=$3
    }
  getline < "maxMove"
  if (($1<maxAtomMove) && ($1>0)) maxAtomMove=$1
  if (maxAtomMove<0.000001) maxAtomMove=0.000001
  }

# record atom velocities for IVR analysis.  This is actually the velocity in the previous run,
```

```
which is the easiest to calculate.
getline < "isomernumber"
isomernum = $1
getline < "runpointnumber"
runpointnum = $1
# routine to control whether NMR calculations are done.
if ((nmrrand==0) && ((runpointnum % nmrevery)==0)) nmrdo=1
if ((nmrrand==1) && (rand()<(1/nmrevery))) nmrdo=1
getline < "uptimelist"
x=1.0001*substr($10,1,3);if (x<8) x=8
# turn of nmrs if load is too high - this is under control of loadlimit parameter in progdyn.conf
and requires proganal to make uptimelist
if ((nmrrand==1) && (x>loadlimit)) nmrdo=0

if (diag==3) print "runpoint ",runpointnum-1,"runisomer ",isomernum >> "vellist"
for (at=1;at<=numAtoms;at++) {
  atomVel=((oldarr[at,1]-olderarr[at,1])^2    +    (oldarr[at,2]-olderarr[at,2])^2    +(oldarr[at,3]-
olderarr[at,3])^2)^.5
  KEold=KEold+0.5*weight[at]*(atomVel^2)/((timestep^2)*conver1)
  if (diag==3) print atomVel >> "vellist"
  }
}

#pull out the potential energy
/SCF Done/ || /EUMP2 =/ || / Energy=/ || /ONIOM:/ {
if (($1=="Energy=") && ($3=="NIter="))  newPotentialE=$2
if ($1=="SCF") newPotentialE=$5
if ($2=="extrapolated")  newPotentialE=$5
if ($1=="E2") {
  tempstring=$6
  split(tempstring, arr10, "D")
  newPotentialE=arr10[1]*(10^arr10[2])
  }
newPotEK=(newPotentialE-potentialE)*627.509
}

#must adjust next line for weird atoms
(/      1    / || /      2    / || /      3    / || /      4    / || /      5    / || /      6    / || /      7    / || /      8
/ || /      9    / || /      10    / || /      11    / || /      12    / || /      13    / || /      14    / || /      15    / || /
16    / || /      17    / || /      18    / || /      19    / || /      20    / || /      21    / || /      22    / || /      23    /
|| /      24    / || /      25    / || /      26    / || /      27    / || /      28    / || /      29    / || /      30    / || /
31    / || /      32    / || /      33    / || /      34    / || /      35    /) && length($3) > 9 {
i=$1
for (j=1;j<=3;j++) {
  forceArr[i,j]=$(2+j)    #the raw units of the forces are Hartree/Bohr
  }
#if    ((diag>1)    &&    (i==1))    print    "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]"    >>
"diagnostics"
```

```
#if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
}

END {
# sanity check - avoids trajectory blow up
for (at=1;at<=numAtoms;at++) {
  if (((oldarr[at,1]-olderarr[at,1])^2)>1) exit
  }
#routine to apply a force to bring atoms within a sphere - note that if atoms are too far outside of a sphere then the force on them will be very large
#unless sphereforce is turned down
if (sphereon==1) {
  sphereforcetotal=0; totalweight=0
  for (i=1;i<=numAtoms;i++) {
    distToOrig=((oldarr[i,1]^2+oldarr[i,2]^2+oldarr[i,3]^2)^.5)
    if (distToOrig>spheresize) {
#originally tried a harmonic restortation to the sphere but this is too big for atoms far outside the sphere
      sphereforce=sphereforceK*(distToOrig-spheresize)
      if (sphereforce>0.01) sphereforce=0.01
      sphereforcetotal=sphereforcetotal+sphereforce
# tried a constant force outside of sphere but am worried about what this means since the potential is discontinuous and steps are discrete
#       sphereforce=sphereforceK

unitX=sphereforce*oldarr[i,1]/distToOrig;unitY=sphereforce*oldarr[i,2]/distToOrig;unitZ=sphereforce*oldarr[i,3]/distToOrig
      forceArr[i,1]=forceArr[i,1]-unitX;forceArr[i,2]=forceArr[i,2]-unitY;forceArr[i,3]=forceArr[i,3]-unitZ
      }
# calculate the density at 0.9*spheresize
    if (distToOrig<0.9*spheresize) {
      totalweight=totalweight+weight[i]
      }
    }
  density=(totalweight/avNum)/((4/3)*pi*(0.9*spheresize*1E-8)^3)
  }
# routine to apply forces between atoms, used for umbrella sampling
# the next few lines are a kludge to apply the force to one of a series of atoms, whichever is closest to afatom[1]
for (i=3;i<8;i++) {
  if (afatom[i]>0) {
    if(Distance(afatom[1],afatom[i])<Distance(afatom[1],afatom[2])) afatom[2]=afatom[i]
    }
  if (afatomB[i]>0) {
    if(Distance(afatomB[1],afatomB[i])<Distance(afatomB[1],afatomB[2])) afatomB[2]=afatomB[i]
    }
```

```
  if (afatomC[i]>0) {
    if(Distance(afatomC[1],afatomC[i])<Distance(afatomC[1],afatomC[2]))
afatomC[2]=afatomC[i]
    }
  }
# applyforce 1 puts a linear constant force.
# applyforce 2 puts on a harmonic restoring force to apforceX0
if (applyforce>0) {
  delX=oldarr[afatom[1],1]-oldarr[afatom[2],1];delY=oldarr[afatom[1],2]-
oldarr[afatom[2],2];delZ=oldarr[afatom[1],3]-oldarr[afatom[2],3];
  distatoms=(delX^2+delY^2+delZ^2)^.5
  if (applyforce==2) apforce=apforce*(distatoms-apforceX0)
  if (applyforce==3) apforce=apforce*(distatoms-apforceX0) + apforce2*(distatoms-
apforceX0)^2
  if (applyforce==4) apforce=apforce*(distatoms-apforceX0) + apforce2*(distatoms-
apforceX0)^2 + apforce3*(distatoms-apforceX0)^3
  unitX=apforce*delX/distatoms;unitY=apforce*delY/distatoms;;unitZ=apforce*delZ/distatoms;
  forceArr[afatom[1],1]=forceArr[afatom[1],1]-
unitX;forceArr[afatom[1],2]=forceArr[afatom[1],2]-
unitY;forceArr[afatom[1],3]=forceArr[afatom[1],3]-unitZ

forceArr[afatom[2],1]=forceArr[afatom[2],1]+unitX;forceArr[afatom[2],2]=forceArr[afatom[2],
2]+unitY;forceArr[afatom[2],3]=forceArr[afatom[2],3]+unitZ
  }
if (applyforceB>0) {
  delX=oldarr[afatomB[1],1]-oldarr[afatomB[2],1];delY=oldarr[afatomB[1],2]-
oldarr[afatomB[2],2];delZ=oldarr[afatomB[1],3]-oldarr[afatomB[2],3];
  distatoms=(delX^2+delY^2+delZ^2)^.5
  if (applyforceB==2) apforceB=apforceB*(distatoms-apforceX0B)
  if (applyforceB==3) apforceB=apforceB*(distatoms-apforceX0B) + apforce2B*(distatoms-
apforceX0B)^2
  if (applyforceB==4) apforceB=apforceB*(distatoms-apforceX0B) + apforce2B*(distatoms-
apforceX0B)^2 + apforce3B*(distatoms-apforceX0B)^3

unitX=apforceB*delX/distatoms;unitY=apforceB*delY/distatoms;;unitZ=apforceB*delZ/distato
ms;
  forceArr[afatomB[1],1]=forceArr[afatomB[1],1]-
unitX;forceArr[afatomB[1],2]=forceArr[afatomB[1],2]-
unitY;forceArr[afatomB[1],3]=forceArr[afatomB[1],3]-unitZ

forceArr[afatomB[2],1]=forceArr[afatomB[2],1]+unitX;forceArr[afatomB[2],2]=forceArr[afato
mB[2],2]+unitY;forceArr[afatomB[2],3]=forceArr[afatomB[2],3]+unitZ
  }
if (applyforceC>0) {
  delX=oldarr[afatomC[1],1]-oldarr[afatomC[2],1];delY=oldarr[afatomC[1],2]-
oldarr[afatomC[2],2];delZ=oldarr[afatomC[1],3]-oldarr[afatomC[2],3];
  distatoms=(delX^2+delY^2+delZ^2)^.5
  if (applyforceC==2) apforceC=apforceC*(distatoms-apforceX0C)
```

```
  if (applyforceC==3) apforceC=apforceC*(distatoms-apforceX0C) + apforce2C*(distatoms-
apforceX0C)^2
  if (applyforceC==4) apforceC=apforceC*(distatoms-apforceX0C) + apforce2C*(distatoms-
apforceX0C)^2 + apforce3C*(distatoms-apforceX0C)^3

unitX=apforceC*delX/distatoms;unitY=apforceC*delY/distatoms;;unitZ=apforceC*delZ/distato
ms;
  forceArr[afatomC[1],1]=forceArr[afatomC[1],1]-
unitX;forceArr[afatomC[1],2]=forceArr[afatomC[1],2]-
unitY;forceArr[afatomC[1],3]=forceArr[afatomC[1],3]-unitZ

forceArr[afatomC[2],1]=forceArr[afatomC[2],1]+unitX;forceArr[afatomC[2],2]=forceArr[afato
mC[2],2]+unitY;forceArr[afatomC[2],3]=forceArr[afatomC[2],3]+unitZ
  }
#routine to slowly move an atom toward the origin as set by a harmonic potential
if (zeroatomon==1) {
  multiple=0.99996
  oldarr[zeroatom,1]=multiple*oldarr[zeroatom,1]
  oldarr[zeroatom,2]=multiple*oldarr[zeroatom,2]
  oldarr[zeroatom,3]=multiple*oldarr[zeroatom,3]
  }
#print out some things to vellist and do thermostat
apparentTemp=KEold*2/(3*RgasK*numAtoms)
# the damping in the thermostat is based on temperature based on old geo vs older geo
if (thermostat==1) {
  if (diag<4) print "KEold",KEold,"desired temperature",temp,"apparent
Temperature",apparentTemp >> "vellist"
  if (apparentTemp>temp) damping=thermostatmult
  if (apparentTemp<temp) damping=1/thermostatmult
  }

##############routine for DRPs###############
if (DRP==1) {
  maxForce=0;oscillTest=0
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then mult time
(s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/(weight[i]/(a
vNum*1000))
      oscillTest=oscillTest+forceArr[i,j]*oldForce[i,j]
      if (forceArr[i,j]>maxForce) maxForce=forceArr[i,j]
      if ((0-forceArr[i,j])>maxForce) maxForce=-forceArr[i,j]
      }
    if (i==1) printf("% .8f % .8f % .8f \n",forceArr[1,1],forceArr[1,2],forceArr[1,3]) >
"oldAdjForces"
    if (i>1) printf("% .8f % .8f % .8f \n",forceArr[i,1],forceArr[i,2],forceArr[i,3]) >>
```

```
"oldAdjForces"
    }
  print "oscillTest ",oscillTest >> "oldAdjForces"
  if (oscillTest<0) {
    maxAtomMove = maxAtomMove*0.5
    print maxAtomMove > "maxMove"
    }
  if (oscillTest>0) {
    maxAtomMove = maxAtomMove*1.2
    print maxAtomMove > "maxMove"
    }
  print "maxAtomMove ",maxAtomMove >> "oldAdjForces"
  forceMult=maxAtomMove/maxForce
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
      newarr[i,j]=oldarr[i,j]+forceMult*forceArr[i,j]
      }
    }
  }
########

##############normal routine for Verlet ##############
if (DRP==0) {
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then mult time
(s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/(weight[i]/(a
vNum*1000))
#           if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
"diagnostics"
#       if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
       newarr[i,j]=oldarr[i,j]+damping*(oldarr[i,j]-olderarr[i,j])+forceArr[i,j]
       if ((i==fixedatom1) || (i==fixedatom2) || (i==fixedatom3) || (i==fixedatom4))
newarr[i,j]=oldarr[i,j]
#turn around atoms outside the box
       if (boxon==1) {
         if (newarr[i,j]>boxsize) if (oldarr[i,j]>olderarr[i,j])
newarr[i,j]=oldarr[i,j]+damping*(olderarr[i,j]-oldarr[i,j])+forceArr[i,j]
         if (newarr[i,j]<-1*boxsize) if (oldarr[i,j]<olderarr[i,j])
newarr[i,j]=oldarr[i,j]+damping*(olderarr[i,j]-oldarr[i,j])+forceArr[i,j]
         }
       }
    }
  for (at=1;at<=numAtoms;at++) {
    atomVel=((oldarr[at,1]-newarr[at,1])^2 + (oldarr[at,2]-newarr[at,2])^2 +(oldarr[at,3]-
newarr[at,3])^2)^.5
```

```
    KEnew=KEnew+0.5*weight[at]*(atomVel^2)/((timestep^2)*conver1)
    }
    KEave=0.5*KEold+0.5*KEnew
    Etotal=newPotEK+KEave
#still basing apparent Temperature on velocities from old vs older, even though the KE now represents an average of old and new
    if (diag==4) print runpointnum,"KEave",KEave,"apparent Temperature",apparentTemp,"newPotEK",newPotEK,"Etotal",Etotal,"TotalSphereForce",sphere forcetotal,"density in 0.9r",density >> "vellist"
  }
########

print "%nproc=" processors
print "%mem=" memory
if (killcheck!=1) print "%chk=" checkpoint
if (nonstandard==0) {
  print "#p " method " force scf=(xqc,maxconven=155,fulllinear,nosym) "
  if (meth2=="unrestricted") print "guess=mix" #for unrestricted calculations
  if (meth2=="read") print "guess=tcheck" #for reading orbitals from check, sometimes faster, sometimes not
  print "pop=none "
  if (length(meth3)>2) print meth3
  if (length(meth4)>2) print meth4
  }
if (nonstandard==1) {
  print "# "
  print "nonstd"
  system("cat nonstandard")
  }
print ""
print  title1,title2,title3,title4
print "runpoint ",runpointnum
print "runisomer ",isomernum
if (DRP==1) print "maxForce and forceMult and maxAtomMove",maxForce,forceMult,maxAtomMove
print ""
if (oniommult==0) print charge,multiplicity
if (oniommult>0) print charge,multiplicity,oniomcharge,oniommult
print numAtoms >> "traj"
print newPotentialE,title1,title2,title3,title4,"runpoint ",runpointnum,"runisomer ",isomernum >> "traj"
for (i=1;i<=numAtoms;i++) {
  printf("%s %.7f %.7f %.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3])
  printf("%s %.7f %.7f %.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3]) >> "traj"
  print "" >> "traj"
  if ((i>highlevel) && (i<=highlevel+linkatoms)) printf(" %s","M H")
  if (i>(highlevel+linkatoms)) printf(" %s","M")
  print ""
```

```
  }
print ""
if (length(meth5)>2) print meth5
if (length(meth6)>2) print meth6
if (methodfilelines>=1) {
  for (i=1;i<=methodfilelines;i++) {
    getline < "methodfile"
    print $0
    }
  }
if ((nmrtype>0) && (nmrdo==1)) {
  print "--link1--"
  print "%nproc=" processors
  print "%mem=" memory
  print "%chk=" checkpoint
  print "# " nmrmethod " nmr=giao geom=check"
  if (nmrmethod==method) print "guess=tcheck"
  if (length(meth7)>2) print meth7
  print ""
  print title1,title2,title3,title4
  print "runpoint ",runpointnum
  print "runisomer ",isomernum
  print ""
  print charge,multiplicity
  }
print ""
if ((nmrtype>1) && (nmrdo==1)) {
  print "--link1--"
  print "%nproc=" processors
  print "%mem=" memory
  print "%chk=" checkpoint
  print "# " nmrmethod2 " nmr=giao geom=check"
  if (length(meth7)>2) print meth7
  print ""
  print title1,title2,title3,title4
  print "runpoint ",runpointnum
  print "runisomer ",isomernum
  print ""
  print charge,multiplicity
  }
print ""
if ((nmrtype>2) && (nmrdo==1)) {
  print "--link1--"
  print "%nproc=" processors
  print "%mem=" memory
  print "%chk=" checkpoint
  print "# " nmrmethod3 " nmr=giao geom=check"
  if (length(meth7)>2) print meth7
```

```
  print ""
  print title1,title2,title3,title4
  print "runpoint ",runpointnum
  print "runisomer ",isomernum
  print ""
  print charge,multiplicity
  }
print ""

if ((nmrcc==1) && (nmrdo==1)) {
  print "CCSD(T) NMR calculation" > "ZMAT"
  for (i=1;i<=numAtoms;i++) {
    printf("%s %.7f %.7f %.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3]) >> "ZMAT"
    print "" >> "ZMAT"
    }
  print "" >> "ZMAT"
  print "*ACES2(CALC=CCSD[T],PROP=NMR,BASIS=dzp" >> "ZMAT"
  print      "ABCDTYPE=AOBASIS,TREAT_PERT=SEQUENTIAL,CC_PROG=ECC"      >>
"ZMAT"
  print "COORD=CARTESIAN" >> "ZMAT"
  print "MEM_UNIT=GB,MEMORY=2)" >> "ZMAT"
  print "" >> "ZMAT"
  }
}

function Distance(Atom1,Atom2) {
 return                                  sqrt((oldarr[Atom1,1]-oldarr[Atom2,1])^2+(oldarr[Atom1,2]-
oldarr[Atom2,2])^2+(oldarr[Atom1,3]-oldarr[Atom2,3])^2)
}
```

Program progcfour

This module calls an outside calculation with CFOUR but was not used for the current paper and its presense is not needed to reproduce the current work. Its listing was published in the SI for a previous paper: Biswas, B.; Singleton, D. A. *J. Am. Chem. Soc.* **2015**, *137*, 14244-14247.

Program randgen.c

This is compiled before use to give the service program *randgen*

```
#include <stdio.h>
#include <stdlib.h>

int a,b,c;
double d;

int product(int x, int y);

int main(void)
{
  int count=1;
```

```
  srand48(time (0));
  while (count<=100000)
  {
    d = drand48();
    printf ("%.20f\n", d);
    count++;
  }
  return 0;
}
```

Program proganal when collecting PMF data

```
BEGIN {
firsttitle=1
getline < "isomernumber"
isomer=$1
}
/ NO2/ {
  if (firsttitle==1) {
    printf("%s %s %s %s %s %s %s  ",$1,$2,$3,$4,$6,$7,$8)
    runpoint=$6
    }
  firsttitle++
  }
/Standard orientation/,/Rotational constants/ {
  if (($1>.5) && ($1<99)) {
    A[$1]=$4;B[$1]=$5;C[$1]=$6
    }
  }
#/before annihilation/ {
#   printf("%s %.5f ",$1,$6)
#   }

END {
  para=Distance(1,16)
  meta=Distance(2,16)
  if (Distance(6,16)<meta) meta=Distance(6,16)
  ortho=Distance(3,16)
  if (Distance(5,16)<ortho) ortho=Distance(5,16)
  ipso=Distance(4,16)
  Opara=Distance(1,17)
  if (Distance(1,18)<Opara) Opara=Distance(1,18)
  Ometa=Distance(2,17)
  if (Distance(2,18)<Ometa) Ometa=Distance(2,18)
  if (Distance(6,17)<Ometa) Ometa=Distance(6,17)
  if (Distance(6,18)<Ometa) Ometa=Distance(6,18)
  Oortho=Distance(3,17)
  if (Distance(3,18)<Oortho) Oortho=Distance(3,18)
  if (Distance(5,17)<Oortho) Oortho=Distance(5,17)
```

```
  if (Distance(5,18)<Oortho) Oortho=Distance(5,18)
  Oipso=Distance(4,17)
  if (Distance(4,18)<Oipso) Oipso=Distance(4,18)
  NitF=Distance(16,19)
  if (Distance(16,21)<NitF) NitF=Distance(16,21)
  if (Distance(16,22)<NitF) NitF=Distance(16,22)
  if (Distance(16,23)<NitF) NitF=Distance(16,23)
  BC=Distance(1,20)
  if (Distance(2,20)<BC) BC=Distance(2,20)
  if (Distance(3,20)<BC) BC=Distance(3,20)
  if (Distance(4,20)<BC) BC=Distance(4,20)
  if (Distance(5,20)<BC) BC=Distance(5,20)
  if (Distance(6,20)<BC) BC=Distance(6,20)
  choice=0
  if ((Opara<Ometa) && (Opara<Oortho) && (Opara<NitF)) choice=1
  if ((Ometa<Opara) && (Ometa<Oortho) && (Ometa<NitF)) choice=2
  if ((Oortho<Ometa) && (Oortho<Opara) && (Oortho<NitF)) choice=3
  if (Ometa<2) choice=2
  if (Oortho<2) choice=3
  if (choice==0) printf("%s %.3f %s %.3f %s %.3f %s %.3f %s %.2f %s %.2f
","p",para,"m",meta,"o",ortho,"i",ipso,"NitForNO",NitF,"BC",BC)
  if (choice==1) printf("%s %.3f %s %.3f %s %.3f %s %.3f %s %.2f %s %.2f
","p",para,"m",meta,"o",ortho,"i",ipso,"Opara",Opara,"BC",BC)
  if (choice==2) printf("%s %.3f %s %.3f %s %.3f %s %.3f %s %.2f %s %.2f
","p",para,"m",meta,"o",ortho,"i",ipso,"Ometa",Ometa,"BC",BC)
  if (choice==3) printf("%s %.3f %s %.3f %s %.3f %s %.3f %s %.2f %s %.2f
","p",para,"m",meta,"o",ortho,"i",ipso,"Oortho",Oortho,"BC",BC)
  if (runpoint>500000) {
    print "Too many points.  XXXXN"
#   system("date > nogo")
    }
  if (para<1.6) {
#   print "para product formed XXXX"
#   system("date > nogo")
    }
  if (meta<1.6) {
#   print "meta product formed XXXX"
#   system("date > nogo")
    }
  if (ortho<1.6) {
#   print "ortho product formed XXXX"
#   system("date > nogo")
    }
  if (ipso<1.6) {
#   print "ipso product formed XXXX"
#   system("date > nogo")
    }
  if (Opara<1.6) {
```

```
#     print "Opara product formed XXXX"
      }
   if (Ometa<1.6) {
#     print "Ometa product formed XXXX"
      }
   if (Oortho<1.6) {
#     print "Oortho product formed XXXX"
      }
   if (Oipso<1.6) {
#     print "Oipso product formed XXXX"
      }
#  if (NitF<1.6) {
#     print "NitF product formed XXXX"
#     system("date > nogo")
#     }
   if ((para>5) && (meta>5) && (ortho>5)) {
#     if ((para<5.2) || (para>5.25)) print "Dissociated to SM XXXX"
      }

   system("date '+%b:%d:%Y %T'")
   system("tail -1 Echeck | grep XXXX")
   }

function Distance(Atom1,Atom2) {
  return sqrt((A[Atom1]-A[Atom2])^2 + (B[Atom1]-B[Atom2])^2 + (C[Atom1]-C[Atom2])^2)
}

function Angle(Atom1,Atom2,Atom3) {
   value=((-
Distance(Atom1,Atom3)^2+Distance(Atom1,Atom2)^2+Distance(Atom2,Atom3)^2)/(2*Distanc
e(Atom1,Atom2)*Distance(Atom2,Atom3)))
   return acos(value)
}

function asin(x) { return (180/3.141592)*atan2(x, sqrt(1-x*x)) }

function acos(x) { return (180/3.141592)*atan2(sqrt(1-x*x), x) }

function atan(x) { return (180/3.141592)*atan2(x,1) }

function Dihedral(Atom1,Atom2,Atom3,Atom4) {
   B1x=A[Atom2]-A[Atom1]
   B1y=B[Atom2]-B[Atom1]
   B1z=C[Atom2]-C[Atom1]
   B2x=A[Atom3]-A[Atom2]
   B2y=B[Atom3]-B[Atom2]
   B2z=C[Atom3]-C[Atom2]
   B3x=A[Atom4]-A[Atom3]
```

```
  B3y=B[Atom4]-B[Atom3]
  B3z=C[Atom4]-C[Atom3]
  modB2=sqrt((B2x^2)+(B2y^2)+(B2z^2))
# yAx is x-coord. etc of modulus of B2 times B1
  yAx=modB2*(B1x)
  yAy=modB2*(B1y)
  yAz=modB2*(B1z)
# CP2 is the crossproduct of B2 and B3
  CP2x=(B2y*B3z)-(B2z*B3y)
  CP2y=(B2z*B3x)-(B2x*B3z)
  CP2z=(B2x*B3y)-(B2y*B3x)
  termY=((yAx*CP2x)+(yAy*CP2y)+(yAz*CP2z))
# CP is the crossproduct of B1 and B2
  CPx=(B1y*B2z)-(B1z*B2y)
  CPy=(B1z*B2x)-(B1x*B2z)
  CPz=(B1x*B2y)-(B1y*B2x)
  termX=((CPx*CP2x)+(CPy*CP2y)+(CPz*CP2z))
 dihed4=(180/3.141592)*atan2(termY,termX)
 return dihed4
}

function killdyn(isomer) {
  system("rm -f dyn")
```

Program proganal when running product-forming trajectories

```
BEGIN {
firsttitle=1
getline < "isomernumber"
isomer=$1
}
/ NO2/ {
  if (firsttitle==1) {
    printf("%s %s %s %s %s %s %s  ",$1,$2,$3,$4,$6,$7,$8)
    printf(" %s %s %s  ",$6,$7,$8) >> "fullDistList"
    runpoint=$6
    }
  firsttitle++
  }
/Standard orientation/,/Rotational constants/ {
  if (($1>.5) && ($1<99)) {
    A[$1]=$4;B[$1]=$5;C[$1]=$6
    }
  }
#/before annihilation/ {
#   printf("%s %.5f ",$1,$6)
#   }

END {
```

```
  para=Distance(1,16)
  meta=Distance(2,16)
  if (Distance(6,16)<meta) meta=Distance(6,16)
  ortho=Distance(3,16)
  if (Distance(5,16)<ortho) ortho=Distance(5,16)
  ipso=Distance(4,16)
  Opara=Distance(1,17)
  if (Distance(1,18)<Opara) Opara=Distance(1,18)
  Ometa=Distance(2,17)
  if (Distance(2,18)<Ometa) Ometa=Distance(2,18)
  if (Distance(6,17)<Ometa) Ometa=Distance(6,17)
  if (Distance(6,18)<Ometa) Ometa=Distance(6,18)
  Oortho=Distance(3,17)
  if (Distance(3,18)<Oortho) Oortho=Distance(3,18)
  if (Distance(5,17)<Oortho) Oortho=Distance(5,17)
  if (Distance(5,18)<Oortho) Oortho=Distance(5,18)
  Oipso=Distance(4,17)
  if (Distance(4,18)<Oipso) Oipso=Distance(4,18)
  NitF=Distance(16,19)
  if (Distance(16,21)<NitF) NitF=Distance(16,21)
  if (Distance(16,22)<NitF) NitF=Distance(16,22)
  if (Distance(16,23)<NitF) NitF=Distance(16,23)
  BC=Distance(1,20)
  if (Distance(2,20)<BC) BC=Distance(2,20)
  if (Distance(3,20)<BC) BC=Distance(3,20)
  if (Distance(4,20)<BC) BC=Distance(4,20)
  if (Distance(5,20)<BC) BC=Distance(5,20)
  if (Distance(6,20)<BC) BC=Distance(6,20)
  if (Distance(6,16)<meta) BC=-BC
  choice=0
  if ((Opara<Ometa) && (Opara<Oortho) && (Opara<NitF)) choice=1
  if ((Ometa<Opara) && (Ometa<Oortho) && (Ometa<NitF)) choice=2
  if ((Oortho<Ometa) && (Oortho<Opara) && (Oortho<NitF)) choice=3
  if (Ometa<2) choice=2
  if (Oortho<2) choice=3
  if (choice==0) printf("%s %.3f %s %.3f %s %.3f %s %.3f %s %.2f %s %.2f
","p",para,"m",meta,"o",ortho,"i",ipso,"NitForNO",NitF,"BC",BC)
  if (choice==1) printf("%s %.3f %s %.3f %s %.3f %s %.3f %s %.2f %s %.2f
","p",para,"m",meta,"o",ortho,"i",ipso,"Opara",Opara,"BC",BC)
  if (choice==2) printf("%s %.3f %s %.3f %s %.3f %s %.3f %s %.2f %s %.2f
","p",para,"m",meta,"o",ortho,"i",ipso,"Ometa",Ometa,"BC",BC)
  if (choice==3) printf("%s %.3f %s %.3f %s %.3f %s %.3f %s %.2f %s %.2f
","p",para,"m",meta,"o",ortho,"i",ipso,"Oortho",Oortho,"BC",BC)
  printf("%s %.3f %s %.3f %s %.3f %s %.3f %s %.3f %s %.3f
","p",para,"m1",Distance(2,16),"o1",Distance(3,16),"i",ipso,"o2",Distance(5,16),"m2",Distance(
6,16)) >> "fullDistList"
  print "" >> "fullDistList"
  if (runpoint>500000) {
```

```
    print "Too many points.  XXXXN"
#    system("date > nogo")
    }
  if (para<1.5) {
    print "para product formed XXXX"
    }
  if (meta<1.5) {
    print "meta product formed XXXX"
    }
  if (ortho<1.5) {
    print "ortho product formed XXXX"
    }
  if (ipso<1.5) {
    print "ipso product formed XXXX"
    }
  if (Opara<1.6) {
    print "Opara product formed XXXX"
    }
  if (Ometa<1.6) {
    print "Ometa product formed XXXX"
    }
  if (Oortho<1.6) {
    print "Oortho product formed XXXX"
    }
  if (Oipso<1.6) {
    print "Oipso product formed XXXX"
    }
#  if (NitF<1.6) {
#    print "NitF product formed XXXX"
#    system("date > nogo")
#    }
  if ((para>5) && (meta>5) && (ortho>5)) {
    print "Dissociated to SM XXXX"
    }

  system("date '+%b:%d:%Y %T'")
  system("tail -1 Echeck | grep XXXX")
  }

function Distance(Atom1,Atom2) {
 return sqrt((A[Atom1]-A[Atom2])^2 + (B[Atom1]-B[Atom2])^2 + (C[Atom1]-C[Atom2])^2)
}

function Angle(Atom1,Atom2,Atom3) {
  value=((-
Distance(Atom1,Atom3)^2+Distance(Atom1,Atom2)^2+Distance(Atom2,Atom3)^2)/(2*Distanc
e(Atom1,Atom2)*Distance(Atom2,Atom3)))
  return acos(value)
```

```
}

function asin(x) { return (180/3.141592)*atan2(x, sqrt(1-x*x)) }

function acos(x) { return (180/3.141592)*atan2(sqrt(1-x*x), x) }

function atan(x) { return (180/3.141592)*atan2(x,1) }

function Dihedral(Atom1,Atom2,Atom3,Atom4) {
  B1x=A[Atom2]-A[Atom1]
  B1y=B[Atom2]-B[Atom1]
  B1z=C[Atom2]-C[Atom1]
  B2x=A[Atom3]-A[Atom2]
  B2y=B[Atom3]-B[Atom2]
  B2z=C[Atom3]-C[Atom2]
  B3x=A[Atom4]-A[Atom3]
  B3y=B[Atom4]-B[Atom3]
  B3z=C[Atom4]-C[Atom3]
  modB2=sqrt((B2x^2)+(B2y^2)+(B2z^2))
# yAx is x-coord. etc of modulus of B2 times B1
  yAx=modB2*(B1x)
  yAy=modB2*(B1y)
  yAz=modB2*(B1z)
# CP2 is the crossproduct of B2 and B3
  CP2x=(B2y*B3z)-(B2z*B3y)
  CP2y=(B2z*B3x)-(B2x*B3z)
  CP2z=(B2x*B3y)-(B2y*B3x)
  termY=((yAx*CP2x)+(yAy*CP2y)+(yAz*CP2z))
# CP is the crossproduct of B1 and B2
  CPx=(B1y*B2z)-(B1z*B2y)
  CPy=(B1z*B2x)-(B1x*B2z)
  CPz=(B1x*B2y)-(B1y*B2x)
  termX=((CPx*CP2x)+(CPy*CP2y)+(CPz*CP2z))
 dihed4=(180/3.141592)*atan2(termY,termX)
 return dihed4
}

function killdyn(isomer) {
  system("rm -f dyn")
}
```

progdyn.conf for running product-forming trajectories after the release of constraints

```
#This is the configuration file for PROGDYN.  This file is read by progdynstarterHP and
# the awk programs proggenHP, prog1stpoint, prog2ndpoint, and progdynb.
#The programs won't read anything past the first blank line,
#and this file must end with a blank line.
#The program has a number of default values but they are unlikely to be what you want.
```

```
#Do not delete lines - rather, comment out lines for unwanted options.
#The values here are read repeatedly and most can be changed in the middle of running jobs
#***The keywords are case sensitive.  The following keywords should always be defined:***
#***method, charge, multiplicity, memory, processors, title
#*** method --The following word is copied exactly to the gaussian input file.
method ONIOM(M062X/6-311G*:PM3)
#To do a nonstandard route, make nonstandard 1.  For normal calcs, use nonstandard 0 or else leave it out.
#Then make a file called "nonstandard" containing the nonstandard route with no extra lines.
nonstandard 0
# NMRoptions As is NMRtype=1 will add a section for an NMR calc at every NMRevery intervals.  If you want to combine the two use nonstandard
#NMRtype 1
#NMRmethod2 B97D/6-31G*
#NMRmethod LC-wPBE/6-31G*
#NMRmethod3 B3LYP/cc-pvtz
#NMRevery 4
#NMRrand 1
#NMRcc 1
#loadlimit 10.0
#geometry linear
rotationmode 0
#*** method2 --The options here are restricted, unrestricted, and read. restricted is the default
#If the method is U..., put unrestricted here and the .com files will have in them guess=mix.
#If you put read here, the .com files will contain guess=tcheck, which sometimes makes things faster, sometimes not.
#The use of read requires a specifically defined checkpoint file name using the keyword checkpoint.
method2 restricted
charge 0
multiplicity 1
oniomchargemult 1 1
processors 3
#*** memory --The following "word" is copied exactly to the gaussian input file after %mem=.
memory 7gb
#*** killcheck and checkpoint -- You can use a specifically defined checkpoint file name by putting
#the name after the keyword checkpoint.  This is necessary if you use the read option with method2.
#Defined checkpoint names are an unnecessary modest hastle and if you do not want to bother, use killcheck 1
killcheck 1
#checkpoint g09.chk
#*** diagnostics -- 0 prints out nothing extra, 1 (default) prints out extra stuff to a
#file "diagnostics", 2 adds more stuff, 3 adds velocities to a file "vellist"
#4 adds the apparent temperature to vellist, but this is meaningless with quasiclassical calculations
diagnostics 4
```

#*** title -- the title keyword must be followed by exactly four words
title NO2+Tol 101CH2Cl2IonP Oniom TrajFrom34
#*** initialdis -- 0 (default) turns off displacement of the normal modes, so that all trajectories start from the same place
and only the energies and signs of the motion in the modes are randomized
1 gives a flat distribution of displacements where all of the possible values are equally likely
2 (recommended) gives a QM-like gaussian distribution of displacements, so that displacements in the middle are more likely that
those at the end by 1/e
initialdis 0
#*** timestep -- this is the time between points in the trajectory. Typical values would be 1E-15 or 0.5E-15 or 0.25E-15
timestep 1E-15
#*** scaling -- this lets you scale the gaussian frequencies by a constant
scaling 1.0
temperature 298.15
#*** thermostat 1 puts in a damping factor so as to bring the classical temperature toward the desired temperature.
#*** use a thermostatmult between 0.95 and 1, typically 0.995, so the damping happens slowly - otherwise there will be
#*** overadjustment in response to random variation
#*** the thermostat is not exact. The second traj point ignores this, so it only applies to later points handled by progdynb.
thermostat 1
thermostatmult 0.999
#*** method3, method4, method5, and method6 -- These keywords let you add extra lines to the gaussian input file.
#method3 and method4 add lines at the top of the input after the lines defining the method, and
#this is useful to implement things like the iop for mPW1k
#method5 and method6 add lines after the geometry, after a blank line of course
#only a single term with no spaces can be added, one per method line. Here are some examples to uncomment if needed
#method3 IOp(3/76=0572004280)
#method3 scrf=(pcm,solvent=ethanol)
#method3 scrf=(pcm,Solvent=dichloromethane)
#add the line below with big structures to get it to put out the distance matrix and the input orientation
method4 iop(2/9=2000)
#method4 iop(3/124=3)
#method4 scrf=(pcm,solvent=dmso,read)
#method5 radii=bondi
#method6
#*** methodfile -- This keyword lets you add more complicated endings to gaussian input files
#such as a gen basis set. Put after the keyword the number of lines in a file you create called
#methodfile that contains the test you want to add to the end of the gaussian input
methodfile 0
#*** numimag --This tells the program the number of imaginary frequencies in the starting structure.

#if 0, treats as ground state and direction of all modes is random
#if 1, motion along the reaction coordinate will start out in the direction defined by searchdir
#if 2, only lowest freq will go direction of searchdir and other imag mode will go in random direction
numimag 0
#*** searchdir -- This keyword says what direction to follow the mode associated with the imaginary frequency.
#The choices are "negative" and "positive". Positive moves in the direction defined in the gaussian frequency calculation
#for the imaginary frequency, while negative moves in the opposite direction. The correct choice can be made either
#by a careful inspection of the normal modes and standard orientation geometry, or by trial and error.
searchdir positive
#*** classical -- for quassiclassical dynamics, the default, use 0. for classical dynamics, use 1
#if there are no normal modes and the velocities are to be generated from scratch, use classical 2
classical 2
#*** DRP, saddlepoint, and maxAtomMove --to run a DRP use 'DRP 1' in the line below, otherwise leave it at 0 or comment it out
#the treatment of starting saddlepoints is not yet implemented so use saddlepoint no
#if DRP shows oscillations then decrease maxAtomMove
#DRP 1
#saddlepoint no
#maxAtomMove 0.01
#*** cannonball -- The program can "fire" a trajectory from a starting position toward a particular target, such as toward
#a ts. To use this, make a file cannontraj with numAtom lines and three numbers per line that defines the vector
#for firing the trajectory, relative to the starting geometry's standard orientation. The number following cannonball sets
#the extra energy being put into the structure in kcal/mol
#cannonball 10
#*** keepevery --This tells the program how often to write the gaussian output file to file dyn, after the first two points.
#Use 1 for most dynamics to start with, but use a higher number to save on disk space or molden loading time.
keepevery 99
#*** highlevel --For ONIOM jobs, the following line states the number of highlevel atoms,
#which must come before the medium level atoms. Use some high value such as 999 if not using ONIOM
highlevel 18
#*** fixedatom1, fixedatom2, fixedatom3, and fixedatom4 - These fix atoms in space.
#Fixing one atom serves no useful purpose and messes things up, while fixing two atoms
#fixes one distance and fixing three has the effect of fixing three distances, not just two
#in current form fixed atoms only are meant to work with no displacements, that is, initialdis=0
#fixedatom1 16
#fixedatom2 1
#fixedatom3 4

#fixedatom4 20
#applyforce 1 lets one push atoms together or appart - a positive force pushes them together
#format is applyforce force - with the units on force the same as in the Gaussian output file
#applyforce 2 or 3 or 4 applys a polynomical force centered at dist0. 2 is just harmonic, 3 is second order, 4 is third order
#format is applyforce 4 forcecoefficient dist0 forcecoefficient2 forcecoefficient3
#then use afatoms to chose the atoms with format afatoms firstatom secondatom [additional atoms]
#applyforce 2 0.1 2.1
#afatoms 16 1 2 3 4 5 6
#applyforceB 2 0.01 5.2
#afatomsB 8 15
#applyforceC 2 0.01 5.2
#afatomsC 8 15
#zeroatom pushes the numbered atom toward the origin with a small harmonic potential - good with boxon when you want to keep the reaction in the center
#zeroatom 16
#*** boxon and boxsize - With boxon 1, a cubic box is set such that atoms that reach the edge
#are reflected back toward the middle. Useful for dynamics with solvent molecules. This is a crude
#implementation that is ok for a few thousand femtoseconds but will not conserve energy long term.
#Set the box size so as to fit the entire initial molecule but not have too much extra room.
#The dimensions of the box are two times the boxsize, e.g. boxsize 7.5 leads to a box that is 15 x 15 x 15 angstroms
#boxon 1
#boxsize 11.2
#*** sphereon and spheresize and sphereforce - uses a force to push atoms within a sphere. notice that if the atom is far outside of
#the sphere then the force is large unless sphereforce is set small
sphereon 1
spheresize 12.9
sphereforce .01
#*** displacements -- This keyword lets you set the initialdis of particular modes by using a series of lines of the format
displacements NumberOfMode InitialDisForThatMode, as in the example below. You should be able to do as many of these as you like
you might consider this for rotations where a straight-line displacement goes wrong at large displacements
The choices for InitialDisForThatMode are 0, 1, 2, and 10, where 10 does the same thing as 0 but is maintained for now because
a previous version of the program had a bug that made 0 not work.
#displacements 2 0
#displacements 3 0
#displacements 4 0
#displacements 5 0
#displacements 6 0
#displacements 7 0

#displacements 8 0
#displacements 9 0
#displacements 10 0
#*** etolerance --This sets the allowable difference between the desired energy in a trajectory and the actual
#energy, known after point 1 from the potential energy + the kinetic energy in the initial velocities.
#The unit is kcal/mol and 1 is a normal value for mid-sized organic systems. For very large and floppy molecules, a larger value
#may be needed, but the value must stay way below the average thermal energy in the molecule (not counting zpe).
#If initialdis is not 0 and few trajectories are being rejected, decrease the value.
etolerance 9999999
#*** controlphase --It is sometimes useful to set the phase of particular modes in the initialization of trajectories.
#The format is controlphase numberOfModeToControl positive or controlphase numberOfModeToControl negative.
#controlphase 2 positive
#*** damping -- The damping keyword lets you add or subtract energy from the system at each point, by multiplying the velocities
#by the damping factor. A damping of 1 has no effect, and since you mostly want to change the energy slowly, normal values range
#from 0.95 to 1.05. The use of damping lets one do simulated annealing - you add energy until the structure is moving enough
#to sample the kinds of possibilities you are interested in, then you take away the energy slowly.
damping 1.000
#at a damping of .9995, the energy is cut in half in 693 points
#*** reversetraj --This keyword sets the trajectories so that both directions from a transition state are explored.
reversetraj true

#updated Aug 9, 2007 to include the possibility of classical dynamics by the keyword classical
#updated Jan 2008 to include fixed atoms, ONIOM jobs, keepevery, and box size
#update Feb 2008 to include methodfile parameter
updated Nov 2008 to allow for start without an initial freq calc using classical = 2
update Aug 2010 to include etolerance, damping controlphase and reversetraj

progdyn.conf for molecular dynamics generation of the PMF

#In this example, the distance between the N of the nitronium and the aromatic carbons is held in the area of 3.1 Å by a harmonic potential – see the keywords applyforce and afatoms.
#This is the configuration file for PROGDYN. This file is read by progdynstarterHP and
the awk programs proggenHP, prog1stpoint, prog2ndpoint, and progdynb.
#The programs won't read anything past the first blank line,
#and this file must end with a blank line.
#The program has a number of default values but they are unlikely to be what you want.
#Do not delete lines - rather, comment out lines for unwanted options.
#The values here are read repeatedly and most can be changed in the middle of running jobs
#***The keywords are case sensitive. The following keywords should always be defined:***

```
#***method, charge, multiplicity, memory, processors, title
#*** method --The following word is copied exactly to the gaussian input file.
method ONIOM(M062X/6-311G*:PM3)
#To do a nonstandard route, make nonstandard 1.  For normal calcs, use nonstandard 0 or else leave it out.
#Then make a file called "nonstandard" containing the nonstandard route with no extra lines.
nonstandard 0
# NMRoptions As is NMRtype=1 will add a section for an NMR calc at every NMRevery intervals.  If you want to combine the two use nonstandard
#NMRtype 1
#NMRmethod2 B97D/6-31G*
#NMRmethod LC-wPBE/6-31G*
#NMRmethod3 B3LYP/cc-pvtz
#NMRevery 4
#NMRrand 1
#NMRcc 1
#loadlimit 10.0
#geometry linear
rotationmode 0
#*** method2 --The options here are restricted, unrestricted, and read. restricted is the default
#If the method is U..., put unrestricted here and the .com files will have in them guess=mix.
#If you put read here, the .com files will contain guess=tcheck, which sometimes makes things faster, sometimes not.
#The use of read requires a specifically defined checkpoint file name using the keyword checkpoint.
method2 restricted
charge 0
multiplicity 1
oniomchargemult 1 1
processors 3
#*** memory --The following "word" is copied exactly to the gaussian input file after %mem=.
memory 7gb
#*** killcheck and checkpoint -- You can use a specifically defined checkpoint file name by putting
#the name after the keyword checkpoint.  This is necessary if you use the read option with method2.
#Defined checkpoint names are an unnecessary modest hastle and if you do not want to bother, use killcheck 1
killcheck 1
#checkpoint g09.chk
#*** diagnostics -- 0 prints out nothing extra, 1 (default) prints out extra stuff to a
#file "diagnostics", 2 adds more stuff, 3 adds velocities to a file "vellist"
#4 adds the apparent temperature to vellist, but this is meaningless with quasiclassical calculations
diagnostics 4
#*** title -- the title keyword must be followed by exactly four words
title NO2+Tol 101CH2Cl2IonP Oniom Eq
#*** initialdis -- 0 (default) turns off displacement of the normal modes, so that all trajectories
```

start from the same place
and only the energies and signs of the motion in the modes are randomized
1 gives a flat distribution of displacements where all of the possible values are equally likely
2 (recommended) gives a QM-like gaussian distribution of displacements, so that displacements in the middle are more likely that
those at the end by 1/e
initialdis 0
#*** timestep -- this is the time between points in the trajectory. Typical values would be 1E-15 or 0.5E-15 or 0.25E-15
timestep 1E-15
#*** scaling -- this lets you scale the gaussian frequencies by a constant
scaling 1.0
temperature 298.15
#*** thermostat 1 puts in a damping factor so as to bring the classical temperature toward the desired temperature.
#*** use a thermostatmult between 0.95 and 1, typically 0.995, so the damping happens slowly - otherwise there will be
#*** overadjustment in response to random variation
#*** the thermostat is not exact. The second traj point ignores this, so it only applies to later points handled by progdynb.
thermostat 1
thermostatmult 0.999
#*** method3, method4, method5, and method6 -- These keywords let you add extra lines to the gaussian input file.
#method3 and method4 add lines at the top of the input after the lines defining the method, and
#this is useful to implement things like the iop for mPW1k
#method5 and method6 add lines after the geometry, after a blank line of course
#only a single term with no spaces can be added, one per method line. Here are some examples to uncomment if needed
#method3 IOp(3/76=0572004280)
method3 scf=(conver=5)
#method3 scrf=(pcm,Solvent=dichloromethane)
#add the line below with big structures to get it to put out the distance matrix and the input orientation
method4 iop(2/9=2000)
#method4 iop(3/124=3)
#method4 scrf=(pcm,solvent=dmso,read)
#method5 radii=bondi
#method6
#*** methodfile -- This keyword lets you add more complicated endings to gaussian input files
#such as a gen basis set. Put after the keyword the number of lines in a file you create called
#methodfile that contains the test you want to add to the end of the gaussian input
methodfile 0
#*** numimag --This tells the program the number of imaginary frequencies in the starting structure.
#if 0, treats as ground state and direction of all modes is random
#if 1, motion along the reaction coordinate will start out in the direction defined by searchdir
#if 2, only lowest freq will go direction of searchdir and other imag mode will go in random

direction
numimag 0
#*** searchdir -- This keyword says what direction to follow the mode associated with the imaginary frequency.
#The choices are "negative" and "positive". Positive moves in the direction defined in the gaussian frequency calculation
#for the imaginary frequency, while negative moves in the opposite direction. The correct choice can be made either
#by a careful inspection of the normal modes and standard orientation geometry, or by trial and error.
searchdir positive
#*** classical -- for quassiclassical dynamics, the default, use 0. for classical dynamics, use 1
#if there are no normal modes and the velocities are to be generated from scratch, use classical 2
classical 2
#*** DRP, saddlepoint, and maxAtomMove --to run a DRP use 'DRP 1' in the line below, otherwise leave it at 0 or comment it out
#the treatment of starting saddlepoints is not yet implemented so use saddlepoint no
#if DRP shows oscillations then decrease maxAtomMove
#DRP 1
#saddlepoint no
#maxAtomMove 0.01
#*** cannonball -- The program can "fire" a trajectory from a starting position toward a particular target, such as toward
#a ts. To use this, make a file cannontraj with numAtom lines and three numbers per line that defines the vector
#for firing the trajectory, relative to the starting geometry's standard orientation. The number following cannonball sets
#the extra energy being put into the structure in kcal/mol
#cannonball 10
#*** keepevery --This tells the program how often to write the gaussian output file to file dyn, after the first two points.
#Use 1 for most dynamics to start with, but use a higher number to save on disk space or molden loading time.
keepevery 99
#*** highlevel --For ONIOM jobs, the following line states the number of highlevel atoms,
#which must come before the medium level atoms. Use some high value such as 999 if not using ONIOM
highlevel 18
#*** fixedatom1, fixedatom2, fixedatom3, and fixedatom4 - These fix atoms in space.
#Fixing one atom serves no useful purpose and messes things up, while fixing two atoms
#fixes one distance and fixing three has the effect of fixing three distances, not just two
#in current form fixed atoms only are meant to work with no displacements, that is, initialdis=0
#fixedatom1 16
#fixedatom2 1
#fixedatom3 4
#fixedatom4 20
#applyforce 1 lets one push atoms together or appart - a positive force pushes them together
#format is applyforce force - with the units on force the same as in the Gaussian output file

#applyforce 2 or 3 or 4 applys a polynomical force centered at dist0. 2 is just harmonic, 3 is second order, 4 is third order
#format is applyforce 4 forcecoefficient dist0 forcecoefficient2 forcecoefficient3
#then use afatoms to chose the atoms with format afatoms firstatom secondatom [additional atoms]
applyforce 2 0.1 3.1
afatoms 16 1 2 3 4 5 6
#applyforceB 2 0.01 5.2
#afatomsB 8 15
#applyforceC 2 0.01 5.2
#afatomsC 8 15
#zeroatom pushes the numbered atom toward the origin with a small harmonic potential - good with boxon when you want to keep the reaction in the center
zeroatom 16
#*** boxon and boxsize - With boxon 1, a cubic box is set such that atoms that reach the edge
#are reflected back toward the middle. Useful for dynamics with solvent molecules. This is a crude
#implementation that is ok for a few thousand femtoseconds but will not conserve energy long term.
#Set the box size so as to fit the entire initial molecule but not have too much extra room.
#The dimensions of the box are two times the boxsize, e.g. boxsize 7.5 leads to a box that is 15 x 15 x 15 angstroms
#boxon 1
#boxsize 11.2
#*** sphereon and spheresize and sphereforce - uses a force to push atoms within a sphere. notice that if the atom is far outside of
#the sphere then the force is large unless sphereforce is set small
sphereon 1
spheresize 12.9
sphereforce .01
#*** displacements -- This keyword lets you set the initialdis of particular modes by using a series of lines of the format
displacements NumberOfMode InitialDisForThatMode, as in the example below. You should be able to do as many of these as you like
you might consider this for rotations where a straight-line displacement goes wrong at large displacements
The choices for InitialDisForThatMode are 0, 1, 2, and 10, where 10 does the same thing as 0 but is maintained for now because
a previous version of the program had a bug that made 0 not work.
#displacements 2 0
#displacements 3 0
#displacements 4 0
#displacements 5 0
#displacements 6 0
#displacements 7 0
#displacements 8 0
#displacements 9 0
#displacements 10 0

#*** etolerance --This sets the allowable difference between the desired energy in a trajectory and the actual
#energy, known after point 1 from the potential energy + the kinetic energy in the initial velocities.
#The unit is kcal/mol and 1 is a normal value for mid-sized organic systems. For very large and floppy molecules, a larger value
#may be needed, but the value must stay way below the average thermal energy in the molecule (not counting zpe).
#If initialdis is not 0 and few trajectories are being rejected, decrease the value.
etolerance 9999999
#*** controlphase --It is sometimes useful to set the phase of particular modes in the initialization of trajectories.
#The format is controlphase numberOfModeToControl positive or controlphase numberOfModeToControl negative.
#controlphase 2 positive
#*** damping -- The damping keyword lets you add or subtract energy from the system at each point, by multiplying the velocities
#by the damping factor. A damping of 1 has no effect, and since you mostly want to change the energy slowly, normal values range
#from 0.95 to 1.05. The use of damping lets one do simulated annealing - you add energy until the structure is moving enough
#to sample the kinds of possibilities you are interested in, then you take away the energy slowly.
damping 1.000
#at a damping of .9995, the energy is cut in half in 693 points
#*** reversetraj --This keyword sets the trajectories so that both directions from a transition state are explored.
reversetraj false

progdyn.conf for quasiclassical trajectories started from a toluene / $NO_2^+BF_4^-$ PCM TS

Here, we are only showing the active keywords.
method ONIOM(M062X/6-311G*:PM3)
rotationmode 2
method2 restricted
charge 0
multiplicity 1
oniomchargemult 1 1
processors 3
memory 7gb
killcheck 1
diagnostics 0
title NO2+Tol PCMtsA Oniom 298dis2
initialdis 2
timestep 1E-15
scaling 1.0
temperature 298.15
method3 scrf=(pcm,Solvent=dichloromethane)
method4 iop(2/9=2000)

methodfile 0
numimag 1
searchdir positive
classical 0
keepevery 99999
highlevel 18
keep the reaction in the center
etolerance 1
damping 1.000
reversetraj true

progdynsam

```
BEGIN {
temp=298.15
if (pt<1) startpoint=6363
if (pt>1) startpoint=pt
line=0
printon=0
pointline=0
secondpoint=0
}

{
line++
if (line==1) numAtoms=$1
pointline++
if (printon==1) {
  if ($1=="H") atWeight[pointline]=1.00783
  if ($1=="C") atWeight[pointline]=12.0000
  if ($1=="B") atWeight[pointline]=10.81
  if ($1=="O") atWeight[pointline]=15.99940
  if ($1=="F") atWeight[pointline]=18.9984
  if ($1=="P") atWeight[pointline]=30.9738
  if ($1=="S") atWeight[pointline]=31.972
  if ($1=="N") atWeight[pointline]=14.0030740
  if ($1=="Al") atWeight[pointline]=26.981
  if ($1=="Cl") atWeight[pointline]=35.4527
  if (($1=="C") || ($1=="H") || ($1=="O") || ($1=="P") || ($1=="N") || ($1=="Cl")  || ($1=="B") ||
($1=="F") || ($1=="S") || ($1=="Al")) {
     Arr0[pointline,0]=$1
     Arr0[pointline,1]=$2
     Arr0[pointline,2]=$3
     Arr0[pointline,3]=$4
     Arr1[pointline,0]=$1
     Arr1[pointline,1]=$2
     Arr1[pointline,2]=$3
     Arr1[pointline,3]=$4
     }
```

```
  }
if (secondpoint==1) {
  if (($1=="C") || ($1=="H") || ($1=="O") || ($1=="P") || ($1=="N") || ($1=="Cl")  || ($1=="B") ||
($1=="F") || ($1=="S") || ($1=="Al")) {
    Arr1[pointline,1]=$2-Arr1[pointline,1]
    Arr1[pointline,2]=$3-Arr1[pointline,2]
    Arr1[pointline,3]=$4-Arr1[pointline,3]
    }
  }
if ($8=="runisomer") {
  pointline=0
  }
if ($7==startpoint) {
  pointline=0
  printon=1
  }
if ($7==startpoint+1) {
  secondpoint=1
  pointline=0
  printon=0
  }
if ($7>startpoint+1) {
  secondpoint=0
  printon=0
  }

}

END {
print numAtoms
for (i=1;i<=numAtoms;i++) {
  print Arr0[i,0],Arr0[i,1],Arr0[i,2],Arr0[i,3],atWeight[i]
  }
conver1=4.184E26
srand()
timestep=1E-15
for (i=1;i<=100;i++) {
  newRand=rand()
  newRand2=rand()
  randArr[i]=newRand
  sign[i]=1
  if (newRand2<0.5) sign[i]=-1
}
for (i=1;i<=numAtoms;i++) {
  if ((Arr1[i,1]==0) && (Arr1[i,2]==0) && (Arr1[i,3]==0)) {
    for (j=1;j<=3;j++) {
      KE=-0.001987*temp*log(1-randArr[3*i+j])
      Vel=sign[3*i+j]*timestep*(2*KE*conver1/atWeight[i])^0.5
```

```
      Arr1[i,j]=Vel
      }
    }
  print Arr1[i,1],Arr1[i,2],Arr1[i,3]
  }
printf("%s %i %i %s ","generated from points",startpoint,startpoint+1,"in a trajectory, so no modes to print out")
system("pwd")
print "Total mode energy desired=",0
for (i=1;i<=700;i++) {
  velsq= Arr1[i,1]^2+Arr1[i,2]^2+Arr1[i,3]^2
  KE=1E30*0.5*atWeight[i]*velsq/conver1
  KE=2.388E3*0.5*atWeight[i]*velsq
  #print i,KE
  }
print ""
}
```

Program progwhere

```
/ 1 run/ {
oldcurrent=""
finishtime=0;changetime=0;changedist=0
switches=0
shortestdistance=10;shortestpara=10;shortestmeta=10;shortestortho=10;shortestipso=10;short=10
oldshortestpara=10;oldshortestmeta=10;oldshortestortho=10;oldshortestipso=10
shortestrecent=10;reboundcount=0
olddist=10;
count18=0;count19=0;count2=0;count21=0;count22=0;count23=0;
}
/run/ {
olddist=dist
if (($9<$11) && ($9<$13) && ($9<$15)) {
  current="                para"
  dist=$9
  if (dist<shortestdistance) shortestdistance=dist
  if (dist<shortestpara) shortestpara=dist
  }
if (($11<$9) && ($11<$13) && ($11<$15)) {
  current="           meta"
  dist=$11
  if (dist<shortestdistance) shortestdistance=dist
  if (dist<shortestmeta) shortestmeta=dist
  }
if (($13<$9) && ($13<$11) && ($13<$15)) {
  current="      ortho"
  dist=$13
  if (dist<shortestdistance) shortestdistance=dist
```

```
  if (dist<shortestortho) shortestortho=dist
  }
if (($15<$9) && ($15<$11) && ($15<$13)) {
  current="ipso"
  dist=$15
  if (dist<shortestdistance) shortestdistance=dist
  if (dist<shortestipso) shortestipso=dist
  }
if ((olddist<2) && (dist>=2)) count2++
if (dist<shortestrecent) shortestrecent=dist
if ((dist>=2.3) && (shortestrecent<2)) {
  reboundcount++
  shortestrecent=10
  }
if (current!=oldcurrent) {
  changetime=$5
  changedist=dist
  startcurrent=""
  if ($5>4) switches++
  print oldcurrent,switches,shortestdistance
  shortestdistance=10
  }
oldcurrent=current
if ($5==4) startcurrent=current
}
/XXX/ {
  print "In XXX routine"
  print "final",current, switches, shortestdistance
  finishtime=$5
  if (startcurrent==current) print "No switch in this trajectory!!!!"
  print "data for last switch","finishtime",finishtime,"changetime",changetime,"difference",finishtime-changetime,"changedist",changedist,"switches",switches
  if (current==" para") {
    short=shortestmeta;if (shortestortho<short) short=shortestortho; if (shortestipso<short) short=shortestipso
    print "shortestmeta",shortestmeta,"shortestortho",shortestortho,"shortestipso",shortestipso,"shortest overall",short
    }
  if (current==" meta") {
    short=shortestpara; if (shortestortho<short) short=shortestortho; if (shortestipso<short) short=shortestipso
    print "shortestpara",shortestpara,"shortestortho",shortestortho,"shortestipso",shortestipso,"shortest overall",short
    }
  if (current==" ortho") {
```

```
    short=shortestpara; if (shortestmeta<short) short=shortestmeta; if (shortestipso<short)
short=shortestipso
    print
"shortestpara",shortestpara,"shortestmeta",shortestmeta,"shortestipso",shortestipso,"shortest
overall",short
    }
  if (current=="ipso") {
    short=shortestpara; if (shortestmeta<short) short=shortestmeta; if (shortestortho<short)
short=shortestortho
    print
"shortestpara",shortestpara,"shortestmeta",shortestmeta,"shortestortho",shortestortho,"shortest
overall",short
    }
  print "count2  ",count2,"  reboundcount  ",reboundcount
  finishtime=0;changetime=0;changedist=0;switches=0
  shortestdistance=10
  print "ended XXX routine"
}
```

Program whamnit

```
cd ~
rm -f ~/regiocount
rm -f n8??/seriesfile*
awk -f ~/progseries n872/dynfollowfile n873/dynfollowfile n874/dynfollowfile
n875/dynfollowfile n876/dynfollowfile n837/dynfollowfile n838/dynfollowfile > n837/seriesfile
awk -f ~/progseries n800/dynfollowfile n810/dynfollowfile n819/dynfollowfile
n820/dynfollowfile n821/dynfollowfile n839/dynfollowfile > n800/seriesfile
awk -f ~/progseries n801/dynfollowfile n811/dynfollowfile n822/dynfollowfile
n840/dynfollowfile n841/dynfollowfile n86?/dynfollowfile > n801/seriesfile
awk -f ~/progseries n854/dynfollowfile n855/dynfollowfile n856/dynfollowfile
n857/dynfollowfile n858/dynfollowfile n859/dynfollowfile > n854/seriesfile
awk -f ~/progseries n802/dynfollowfile n812/dynfollowfile n823/dynfollowfile > n802/seriesfile
awk -f ~/progseries n803/dynfollowfile n813/dynfollowfile n824/dynfollowfile
n842/dynfollowfile > n803/seriesfile
awk -f ~/progseries n804/dynfollowfile n814/dynfollowfile n825/dynfollowfile > n804/seriesfile
awk -f ~/progseries n805/dynfollowfile n815/dynfollowfile n826/dynfollowfile > n805/seriesfile
awk -f ~/progseries n806/dynfollowfile n816/dynfollowfile n827/dynfollowfile > n806/seriesfile
awk -f ~/progseries n807/dynfollowfile n817/dynfollowfile n828/dynfollowfile > n807/seriesfile
awk -f ~/progseries n808/dynfollowfile n829/dynfollowfile > n808/seriesfile
awk -f ~/progseries n809/dynfollowfile n830/dynfollowfile > n809/seriesfile
awk -f ~/progseries n831/dynfollowfile n832/dynfollowfile > n831/seriesfile
awk -f ~/progseries n833/dynfollowfile n834/dynfollowfile > n833/seriesfile
awk -f ~/progseries n835/dynfollowfile n836/dynfollowfile > n835/seriesfile
cd ~/wham/wham
./wham 1.475 5.675 84 0.000001 298.15 0 metadatafile.nitrations ~/output.nitrationfull 6 23
cd
cat output.nitrationfull
cat ~/regiocount
```

cat ~/wham/wham/metadatafile.nitrations

Program progseries

```
BEGIN {
countpara=0;countmeta=0;countortho=0;countipso=0;counttotal=0
oldfilename=""
switches=-1
current="";oldclosest=""
currentop=""
oldop=""
opswitches=-1
}
/run/ {
if (oldfilename!=FILENAME) {
  if (counttotal>0) {
    pp=int(.5+100*countpara/counttotal)
    pm=int(.5+100*countmeta/counttotal)
    po=int(.5+100*countortho/counttotal)
    pi=int(.5+100*countipso/counttotal)
    print  oldfilename," ",countpara,countmeta,countortho,countipso," ",counttotal,"
",pp,pm,po,pi,"  switches",switches,"  opswitches",opswitches >> "regiocount"
    }
  if (counttotal==0) print "" >> "regiocount"
  countpara=0;countmeta=0;countortho=0;countipso=0;counttotal=0;switches=-
1;current="";oldclosest="";opswitches=-1;oldop="";currentop=""
  }
oldfilename=FILENAME
counttotal++
if (($9<$11) && ($9<$13) && ($9<$15)) {
  countpara++
  current="para"
  currentop="para"
  }
if (($11<$9) && ($11<$13) && ($11<$15)) {
  countmeta++
  current="meta"
  }
if (($13<$9) && ($13<$11) && ($13<$15)) {
  countortho++
  current="ortho"
  currentop="ortho"
  }
if (($15<$9) && ($15<$11) && ($15<$13)) {
  countipso++
  current="ipso"
  }
if (current!=oldclosest) switches++
if (currentop!=oldop) opswitches++
```

```
oldclosest=current; oldop=currentop
dist=$9
if ($11<dist) dist=$11
if ($13<dist) dist=$13
if ($15<dist) dist=$15
printf("%.1f %.3f",$5,dist)
print ""
}
END {
if (counttotal>0) {
  pp=int(.5+100*countpara/counttotal)
  pm=int(.5+100*countmeta/counttotal)
  po=int(.5+100*countortho/counttotal)
  pi=int(.5+100*countipso/counttotal)
  }
print  oldfilename,"            ",countpara,countmeta,countortho,countipso,"          ",counttotal,"
",pp,pm,po,pi,"    switches",switches,"  opswitches",opswitches >> "regiocount"
}
```

Program prog3dpath

```
BEGIN {
A[1]=0.0;B[1]=-1.403;C[1]=-8
A[2]=1.198;B[2]=-.695;C[2]=-8
A[3]=1.198;B[3]=.695;C[3]=-8
A[4]=0.0;B[4]=1.403;C[4]=-8
A[5]=1.0;B[5]=0;C[5]=-5
A[6]=-1.198;B[6]=.695;C[6]=-8
A[7]=-1.198;B[7]=-.695;C[7]=-8
}
/run/ {
olderA=oldA;olderB=oldB;olderC=oldC
oldA=A[5];oldB=B[5];oldC=C[5]
delta=.1
optx=0;opty=0;optz=0
dp=$9;dm=$11;dor=$13;di=$15
if ((Error())^.5<delta) delta=(Error())^.5
#print "target distances",dp,dm,dor,di
#print "initial distances",Distance(1,5),Distance(2,5),Distance(3,5),Distance(4,5),"error",Error()
for (i=1;i<=14;i++) {
  olderror=Error()
  while (optz==0) {
    C[5]=C[5]+delta
    if (Error()>olderror) {
      optz=1
      }
    olderror=Error()
    }
  while (opty==0) {
```

```
    B[5]=B[5]+delta
    if (Error()>olderror) {
      opty=1
      }
    olderror=Error()
    }
  while (optx==0) {
    A[5]=A[5]+delta
    if (Error()>olderror) {
      optx=1
      }
    olderror=Error()
    }
  #print "x,y,z after passes",A[5],B[5],C[5]
#                                                    print                    "intermediate
distances",Distance(1,5),Distance(2,5),Distance(3,5),Distance(4,5),"error",Error(),i
  delta=-.5*delta
  optx=0;opty=0;optz=0
  }
countsinceflip++
secondderiv=olderA+A[5]-2*oldA
if ((secondderiv>.015) || (secondderiv<-.015)) {
  if ((A[5]<.05) && (A[5]>-.05) && (countsinceflip>10)) {
    A[2]=-A[2];A[3]=-A[3];A[6]=-A[6];A[7]=-A[7];
    A[5]=-A[5]
    countsinceflip=0
    print
"XXXX
```

```
print "" >> "tempB"
print "" >> "tempC"
}

function Distance(Atom1,Atom2) {
 return sqrt((A[Atom1]-A[Atom2])^2 + (B[Atom1]-B[Atom2])^2 + (C[Atom1]-C[Atom2])^2)
}

function Error() {
#    if (Distance(6,5)<Distance(3,5)) return (dp-Distance(1,5))^2+(dm-Distance(7,5))^2+(dor-
Distance(6,5))^2+(di-Distance(4,5))^2
  return                    (dp-Distance(1,5))^2+(dm-Distance(2,5))^2+(dor-Distance(3,5))^2+(di-
Distance(4,5))^2
}
```

Program Suite PROGMC

PROGMC is a new program created to run efficient Monte Carlo calculations on the system containing toluene / $NO_2^+BF_4^-$ / 101 CH_2Cl_2 system. Aspects of the program are recognizably *ad hoc*, but we envision that future modifications of the program will be usable on diverse systems.

A full listing of the subprograms of PROGMC is given below. To allow the reader to understand or make use of PROGMC, we describe here first the overall structure of the program.

The master control program for Monte Carlo, in the form of a Unix Shell Script, is called *progMC*. For a user to start to use *progMC*, some early lines in it that assign the scratch space and the location of the program files and input files would have to be modified for the local environment. These lines are between lines 12 and 21 and should be apparent. The location of the scratch space is usually passed to *progMC* as a parameter.

progMC takes as input files:
geo - This file contains the initial geometry at the beginning and later the current accepted geometry. Its format is line1: number of atoms; line 2: optional, often contains a title; line 3-end: the atoms and there positions in Cartesian coordinates. Here is an example:

```
18
  NO2+Tol  101CH2Cl2IonP  Oniom  MonteCarlo  runpoint  31398
C -1.2617403 0.1734595 1.7107956
C -0.2553121 -0.5054263 2.4640648
C 0.5521703 0.2290144 3.3654142
C 0.3782197 1.6373306 3.4257961
C -0.5518774 2.3254313 2.5924738
C -1.3446008 1.5460692 1.7229427
C 1.1698044 2.4529314 4.3843350
H -1.8962769 -0.4103785 1.0535189
H -0.2796489 -1.5907112 2.3450544
H 1.1595708 -0.3281763 4.1250153
H -0.6235700 3.3948345 2.5621955
H -2.1326424 1.9681938 1.0652780
H 1.2599393 2.0587910 5.4511793
```

H 0.9502583 3.4864759 4.4010777
H 2.2661395 2.3883560 4.0664127
N 0.1562194 0.6631665 -0.0922596
O 1.1591170 1.0349781 0.2849730
O -0.5782311 0.4442340 -0.9938770

progmc.conf – This is a file giving a variety of configuration options, called on by many of the subprograms. A progmc.conf example is listed below and contains explanations of the program options.

progMC calls the following programs:
progmcb - An awk program that takes random steps from geo and generates subsequent Gaussian input files

progEcheck – This awk program pulls the energy from Gaussian output files, adjusts the energy by any biasing potentials or the potential that holds the sphere of molecules together, and decides if the new energy and geometry should be accepted.

proganal – A program to analyze the latest point and extract data. This program must be redone for each new system. proganal creates the output to mcfollowfile

progMC has the following output files:
runpointnumber – a running tab of the point in the chain of geometries
Elist – a list of all accepted energies
energy – the latest energy
testgeo – the latest test geometry. If the energy of testgeo is accepted, testgeo is moved to geo
latestmcrun and latestmcrun2 – the Gaussian output file from the latest and previously accepted points
mcfollowfile – the output from proganal, records selected data from the successful points but not the unsuccessful points
traj – a file containing the full set of accepted geometries for a Monte Carlo run
vellist – output containing the density of the sphere and the amount of energy used to maintain the sphere, for each successful point
A number of files starting with *'temp'* are created then later erased.

The following helper programs were used for the current study.
whamnitmc – a shell script that extracts data from the mcfollowfile files, sets up and runs wham to calculate the PMF, and keeps track of some general aspects of trajectories
progseriesmc – an AWK script used by whamnitmv to extract data from the mcfollowfile files
wham – a program from Grossfield, Alan, "WHAM: the weighted histogram analysis method", version 2.0.9, http://membrane.urmc.rochester.edu/content/wham that performs the wham analysis

Program progMC

```
#!/bin/bash
#progMC started 12/21/2015
#                              OUTLINE
# A. initilize to perform Gaussian jobs, set the scratch, program, and other directores, remove
```

```
errant control files
# B. use progmcb to read in the geometry from file geo.  progmcb then generates a new point and sets up g09.com
# C. progEcheck then checks to see if the new geometry is acceptable, based on new energy versus energy in file energy
#    If this is the first point, the energy is assigned as huge so the next point is accepted
#     If the new point is accepted then the new point is placed in file geo and the new energy is placed in file energy and proganal is run
# D. go to B
#
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
#origdir, randdir, scratchdir, g09root, logfile all may need varied from system to system and assigned here or by program calling this one
export LC_ALL=C
echo $1
scratchdir=$1
export g09root=/software/lms/g09_D01
. $g09root/g09/bsd/g09.profile
origdir=`pwd`
cd $origdir
logfile=docslog
randdir=~/bin
proggramdir=~/binmc
echo
echo ORIGDIR at the beginning of run:
echo $origdir
ls $origdir
echo
echo SCRATCHDIR at the beginning of run:
echo $scratchdir
ls $scratchdir
echo
echo PROGGRAMDIR at the beginning of run::
echo $proggramdir
ls $proggramdir

rm -f nogo    # assume that if someone is starting a job, they want it to go.
rm -f diagnostics goingwell tempdone # diagnostics contains extra info from previous runs, other two files are from older versions of progdyn

cd $origdir
if (test -s runpointnumber) then
  echo "skipping start and continuing from previous runs"
else
  echo 1 > runpointnumber
fi
```

```
if (test -f energy) then
  echo "we have an energy in place"
  cat energy
else
  echo 9999999999999 > energy
fi
if (test -s progmc.conf) then
  echo "we have a progmc.conf"
else
  echo "no progmc.conf"
  exit 9
fi
if (test -s g09.com) then
  sed -i '/guess=tcheck/d' g09.com      # no chk file on first point
fi
rm -f latestmcrun   # just using this as a signal that we are on the first point of submission

while (true)
do
#
BBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBB
BBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBB
BBBBBBBBBBBBBBBBBBB
  rm -f $scratchdir/goingwell $scratchdir/goodenergy
  cd $origdir
  if (test -s latestmcrun) then
    awk -f $proggramdir/progmcb geo > g09.com
  else
    awk -f $proggramdir/progmcb geo > g09.com
    sed -i '/guess=tcheck/d' g09.com      # no chk file on first point
  fi
  if (test -s g09.com) then
    cd $scratchdir
    cp $origdir/g09.com $scratchdir/g09.com
    $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
    cd $origdir
    grep 'Normal termination' $scratchdir/g09.log > $scratchdir/goingwell
  else
    echo "g09.com not generated"
    break
  fi
  if (test -s $scratchdir/goingwell) then
    cp $scratchdir/g09.log latestmcrun
  else
    echo "some problem in middle of gaussian job"
    cp $scratchdir/g09.log $origdir/g09.log
    break
  fi
```

```
#
CCCC
```

```
# do not change these - rather, change progmc.conf to set the parameters
temp=0.0;memory=20000000;
diag=1; checkpoint="g09.chk"; boxon=0
boxsize=10; title1="you"; title2="need"
title3="a"; title4="progmc.conf"; processors=1; highlevel=99999; linkatoms=0
nonstandard=0
oniomcharge=0; oniommult=0
applypotential=0; zeroatomon=0
sphereon=0; spheresize=999; sphereforceK=0.01
moleculecount=0

#initialization
srand(PROCINFO["pid"])
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447; pi=3.14159265359
numAtoms=0; atomnumber=0
conver1=4.184E26 #dividing by this converts amu angs^2 /s^2 to kcal/mol
OFS="   "

# read progdyn.conf for configuration info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progmc.conf"
  if ($1=="method") method=$2
  if ($1=="method2") meth2=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="oniomchargemult") {
    oniomcharge=$2
    oniommult=$3
    }
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="temperature") temp=$2
  if ($1=="mcstepsize") mcstep=$2
  if ($1=="lengthstep") lengthstep=$2
  if ($1=="anglestep") anglestep=$2
  if ($1=="mcmolrotangle") mcmolrotangle=$2
  if ($1=="molecule") {
    moleculecount++
    molAtoms[moleculecount]=NF-2
    for (i=1;i<NF-1;i++) {
      molecule[moleculecount,i]=$(i+1)
      }
    molStep[moleculecount]=$NF
```

```
    }
  if ($1=="method3") meth3=$2
  if ($1=="method4") meth4=$2
  if ($1=="method5") meth5=$2
  if ($1=="method6") meth6=$2
  if ($1=="method7") meth7=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="linkatoms") linkatoms=$2
  if ($1=="boxon") boxon=$2
  if ($1=="boxsize") boxsize=$2
  if ($1=="sphereon") sphereon=$2
  if ($1=="spheresize") spheresize=$2
  if ($1=="sphereforce") sphereforceK=$2
  if ($1=="methodfile") methodfilelines=$2
  if ($1=="killcheck") killcheck=$2
  if ($1=="nonstandard") nonstandard=$2
  if ($1=="applypotential") {
    apforce=$2; apforceX0=$3
    }
  if ($1=="apatoms") {
    for (i=1;i<8;i++) {
      if ($(i+1)>0) apatom[i]=$(i+1)
      }
    }
  if ($1=="applypotentialplane") {
    apforceplane=$2; apforceplaneX0=$3
    }
  if ($1=="applaneatoms") {
    for (i=1;i<8;i++) {
      if ($(i+1)>0) afplaneatoms[i]=$(i+1)
      }
    }
  if ($1=="zeroatom") {
    zeroatomon=1
    zeroatom=$2
    zeroatompotential=$3
    }
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
    }
  blankLineTester=length($0)
  }

#for (i=1;i<=moleculecount;i++) {
#   for (j=1;j<=molAtoms[i];j++) {
```

```
#     print molecule[i,j]
#     }
#   print molStep[i]
#   }

if (diag>=1) print "***************** starting progdynb *****************" >>
"diagnostics"
if (diag>=1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag>=1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag>=1) print "processors,checkpoint,title" >> "diagnostics"
if (diag>=1) print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"

# get number of atoms and geometry from file geo
getline <  "geo"
numAtoms=$1
getline < "geo"
for (i=1;i<=numAtoms;i++) {
  getline < "geo"
  atSym[i]=$1
  oldarr[i,1]=$2; oldarr[i,2]=$3; oldarr[i,3]=$4
  if (atSym[i]=="H") atRadius[i]=1.2
  if (atSym[i]=="B") atRadius[i]=1.8
  if (atSym[i]=="C") atRadius[i]=1.7
  if (atSym[i]=="N") atRadius[i]=1.55
  if (atSym[i]=="O") atRadius[i]=1.52
  if (atSym[i]=="F") atRadius[i]=1.47
  if (atSym[i]=="Cl") atRadius[i]=1.75
  }

# record atom velocities for IVR analysis.  This is actually the velocity in the previous run,
which is the easiest to calculate.
getline < "runpointnumber"
runpointnum = $1
}

#pull out the potential energy
/SCF Done/ || /EUMP2 =/ || / Energy=/ || /ONIOM:/ {
  if (($1=="Energy=") && ($3=="NIter="))  newPotentialE=$2
  if ($1=="SCF") newPotentialE=$5
  if ($2=="extrapolated")  newPotentialE=$5
  if ($1=="E2") {
    tempstring=$6
    split(tempstring, arr10, "D")
    newPotentialE=arr10[1]*(10^arr10[2])
    }
  newPotEK=(newPotentialE-potentialE)*627.509
  }
```

```
END {
# idea for moving atoms within molecules - define each atom by a vector vs its nearest neighbor,
displace by changing
# the length of the vector and by moving it in two orthogonal directions
for (k=1;k<=moleculecount;k++) {
#  print atSym[molecule[k,1]]
  for (i=2;i<=molAtoms[k];i++) {
    atCon[i]=i-1
    for (m=1;m<i-1;m++) {
      if    (Distance(molecule[k,m],molecule[k,i])<Distance(molecule[k,atCon[i]],molecule[k,i]))
atCon[i]=m
      }
    vector[i,1]=oldarr[molecule[k,i],1]-oldarr[molecule[k,atCon[i]],1]
    vector[i,2]=oldarr[molecule[k,i],2]-oldarr[molecule[k,atCon[i]],2]
    vector[i,3]=oldarr[molecule[k,i],3]-oldarr[molecule[k,atCon[i]],3]
#    print atSym[molecule[k,i]],atCon[i],vector[i,1],vector[i,2],vector[i,3]
# now make one unit vector that is perpendicular to the first vector
    pervector1[i,1]=vector[i,2]/((vector[i,1]^2+vector[i,2]^2)^.5)
    pervector1[i,2]=-vector[i,1]/((vector[i,1]^2+vector[i,2]^2)^.5)
    pervector1[i,3]=0
#    print "perpendicular unit vector",pervector1[i,1],pervector1[i,2],pervector1[i,3]`
# now make another unit vector perpendicular to both
    pervector2[i,1]=vector[i,2]*pervector1[i,3]-vector[i,3]*pervector1[i,2]
    pervector2[i,2]=vector[i,3]*pervector1[i,1]-vector[i,1]*pervector1[i,3]
    pervector2[i,3]=vector[i,1]*pervector1[i,2]-vector[i,2]*pervector1[i,1]
    norm=(pervector2[i,1]^2+pervector2[i,2]^2+pervector2[i,3]^2)^.5

pervector2[i,1]=pervector2[i,1]/norm;pervector2[i,2]=pervector2[i,2]/norm;pervector2[i,3]=perv
ector2[i,3]/norm;
#    print "2nd perpendicular unit vector",pervector2[i,1],pervector2[i,2],pervector2[i,3]`
    stepL=2*(rand()-.5)*lengthstep
    step1=2*(rand()-.5)*anglestep
    step2=2*(rand()-.5)*anglestep
    if (molecule[k,i]<7) {
      step1=step1/5;step2=step2/5;stepL=stepL/5
      }

vector[i,1]=vector[i,1]+step1*pervector1[i,1]+step2*pervector2[i,1]+stepL*vector[i,1]/Distance(
molecule[k,atCon[i]],molecule[k,i])

vector[i,2]=vector[i,2]+step1*pervector1[i,2]+step2*pervector2[i,2]+stepL*vector[i,2]/Distance(
molecule[k,atCon[i]],molecule[k,i])

vector[i,3]=vector[i,3]+step1*pervector1[i,3]+step2*pervector2[i,3]+stepL*vector[i,3]/Distance(
molecule[k,atCon[i]],molecule[k,i])
#    print "newvector",atSym[molecule[k,i]],atCon[i],vector[i,1],vector[i,2],vector[i,3]
    }
# now we convert back to exteranl cartesian coordinates
```

```
# atom 1 is just at its original position
#                                                
```

```
"tempradius"
# figure out the angle to rotate around x, y, and z axes, in radians
  angleX=pi*mcmolrotangle*2*(rand()-.5)/180
  angleY=pi*mcmolrotangle*2*(rand()-.5)/180
  angleZ=pi*mcmolrotangle*2*(rand()-.5)/180
  maxDistToX=0;maxDistToY=0;maxDistToZ=0
  for (i=1;i<=molAtoms[k];i++) {
# change coordinates to center of mass
    CMgeo[k,i,1]=newarr[molecule[k,i],1]-CM[k,1]
    CMgeo[k,i,2]=newarr[molecule[k,i],2]-CM[k,2]
    CMgeo[k,i,3]=newarr[molecule[k,i],3]-CM[k,3]
    if                                          ((CMgeo[k,i,2]^2+CMgeo[k,i,3]^2)^.5>maxDistToX)
maxDistToX=(CMgeo[k,i,2]^2+CMgeo[k,i,3]^2)^.5
    if                                          ((CMgeo[k,i,1]^2+CMgeo[k,i,3]^2)^.5>maxDistToY)
maxDistToY=(CMgeo[k,i,1]^2+CMgeo[k,i,3]^2)^.5
    if                                          ((CMgeo[k,i,1]^2+CMgeo[k,i,2]^2)^.5>maxDistToZ)
maxDistToZ=(CMgeo[k,i,1]^2+CMgeo[k,i,2]^2)^.5
# figure out how big the molecule is.  We will rotate big molecules less and small ones more.
    }
#  print maxDistToX,maxDistToY,maxDistToZ > "tempradius"
#cut rotation angle if molecule is bigger to 2 angs radius
  if (maxDistToX>1.6) angleX=angleX*1.6/maxDistToX
  if (maxDistToY>1.6) angleY=angleY*1.6/maxDistToY
  if (maxDistToZ>1.6) angleZ=angleZ*1.6/maxDistToZ
#now apply the rotation
  for (i=1;i<=molAtoms[k];i++) {
# first x
    tempvar=CMgeo[k,i,2]*cos(angleX)-CMgeo[k,i,3]*sin(angleX)
    CMgeo[k,i,3]=CMgeo[k,i,2]*sin(angleX)+CMgeo[k,i,3]*cos(angleX)
    CMgeo[k,i,2]=tempvar
# then y
    tempvar=CMgeo[k,i,1]*cos(angleY)+CMgeo[k,i,3]*sin(angleY)
    CMgeo[k,i,3]=-CMgeo[k,i,1]*sin(angleY)+CMgeo[k,i,3]*cos(angleY)
    CMgeo[k,i,1]=tempvar
# then z
    tempvar=CMgeo[k,i,1]*cos(angleZ)-CMgeo[k,i,2]*sin(angleZ)
    CMgeo[k,i,2]=CMgeo[k,i,1]*sin(angleZ)+CMgeo[k,i,2]*cos(angleZ)
    CMgeo[k,i,1]=tempvar
#now restore to external coordinates
    newarr[molecule[k,i],1]=CMgeo[k,i,1]+CM[k,1]
    newarr[molecule[k,i],2]=CMgeo[k,i,2]+CM[k,2]
    newarr[molecule[k,i],3]=CMgeo[k,i,3]+CM[k,3]
    #print newarr[molecule[k,i],1],newarr[molecule[k,i],2],newarr[molecule[k,i],3]
    }
  }

print "%nproc=" processors
print "%mem=" memory
```

```
if (killcheck!=1) print "%chk=" checkpoint
if (nonstandard==0) {
  print "#p " method " scf=(xqc,maxconven=155,fulllinear,nosym) "
  if (meth2=="unrestricted") print "guess=mix" #for unrestricted calculations
  if (meth2=="read") print "guess=tcheck" #for reading orbitals from check, sometimes faster,
sometimes not
  print "pop=none "
  if (length(meth3)>2) print meth3
  if (length(meth4)>2) print meth4
  }
if (nonstandard==1) {
  print "# "
  print "nonstd"
  system("cat nonstandard")
  }
print ""
print  title1,title2,title3,title4
print "runpoint ",runpointnum
print ""
if (oniommult==0) print charge,multiplicity
if (oniommult>0) print charge,multiplicity,oniomcharge,oniommult
print numAtoms > "testgeo"
print newPotentialE,title1,title2,title3,title4,"runpoint ",runpointnum >> "testgeo"
for (i=1;i<=numAtoms;i++) {
  printf("%s %.7f %.7f %.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3])
  printf("%s %.7f %.7f %.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3]) >> "testgeo"
  print "" >> "testgeo"
  if ((i>highlevel) && (i<=highlevel+linkatoms)) printf(" %s","M H")
  if (i>(highlevel+linkatoms)) printf(" %s","M")
  print ""
  }
print ""
if (length(meth5)>2) print meth5
if (length(meth6)>2) print meth6
if (methodfilelines>=1) {
  for (i=1;i<=methodfilelines;i++) {
    getline < "methodfile"
    print $0
    }
  }
}

function Distance(Atom1,Atom2) {
 return                                  sqrt((oldarr[Atom1,1]-oldarr[Atom2,1])^2+(oldarr[Atom1,2]-
oldarr[Atom2,2])^2+(oldarr[Atom1,3]-oldarr[Atom2,3])^2)
}

function Angle(Atom1,Atom2,Atom3) {
```

```
  value=((-
Distance(Atom1,Atom3)^2+Distance(Atom1,Atom2)^2+Distance(Atom2,Atom3)^2)/(2*Distanc
e(Atom1,Atom2)*Distance(Atom2,Atom3)))
  return acos(value)
}

function asin(x) { return (180/3.141592)*atan2(x, sqrt(1-x*x)) }

function acos(x) { return (180/3.141592)*atan2(sqrt(1-x*x), x) }

function atan(x) { return (180/3.141592)*atan2(x,1) }

function Dihedral(Atom1,Atom2,Atom3,Atom4) {
  B1x=oldarr[Atom2,1]-oldarr[Atom1,1]
  B1y=oldarr[Atom2,2]-oldarr[Atom1,2]
  B1z=oldarr[Atom2,3]-oldarr[Atom1,3]
  B2x=oldarr[Atom3,1]-oldarr[Atom2,1]
  B2y=oldarr[Atom3,2]-oldarr[Atom2,2]
  B2z=oldarr[Atom3,3]-oldarr[Atom2,3]
  B3x=oldarr[Atom4,1]-oldarr[Atom3,1]
  B3y=oldarr[Atom4,2]-oldarr[Atom3,2]
  B3z=oldarr[Atom4,3]-oldarr[Atom3,3]
  modB2=sqrt((B2x^2)+(B2y^2)+(B2z^2))
# yAx is x-coord. etc of modulus of B2 times B1
  yAx=modB2*(B1x)
  yAy=modB2*(B1y)
  yAz=modB2*(B1z)
# CP2 is the crossproduct of B2 and B3
  CP2x=(B2y*B3z)-(B2z*B3y)
  CP2y=(B2z*B3x)-(B2x*B3z)
  CP2z=(B2x*B3y)-(B2y*B3x)
  termY=((yAx*CP2x)+(yAy*CP2y)+(yAz*CP2z))
# CP is the crossproduct of B1 and B2
  CPx=(B1y*B2z)-(B1z*B2y)
  CPy=(B1z*B2x)-(B1x*B2z)
  CPz=(B1x*B2y)-(B1y*B2x)
  termX=((CPx*CP2x)+(CPy*CP2y)+(CPz*CP2z))
 dihed4=(180/3.141592)*atan2(termY,termX)
 return dihed4
}
```

Program progEcheck

```
BEGIN {
#Dec 21 2015
#This program pulls out the energy from latestmcrun and it pulls the energy from file energy
#and it applies the Monte Carlo test to see if the new point is accepted.  If so, it makes a file
"goodenergy"
```

```
#some default parameters
apforce[1]=0;apatom[1,1]=0;apatom[1,2]=0;
sphereon=0;spheresize=99999;sphereforce=0
zeroatom=0;zeroatomforceK=0.1
potentialcount=0; planeradius=1.4

#initialization
srand(PROCINFO["pid"])
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447; pi=3.14159265359
pi=3.141592
numAtoms=0; atomnumber=0
conver1=4.184E26 #dividing by this converts amu angs^2 /s^2 to kcal/mol
OFS="   "

# read progdyn.conf for configuration info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progmc.conf"
  if ($1=="temperature") temp=$2
  if ($1=="zeroatom") {
    zeroatomon=1
    zeroatom=$2
    zeroatomforceK=$3
    }
  if ($1=="sphereon") sphereon=$2
  if ($1=="spheresize") spheresize=$2
  if ($1=="sphereforce") sphereforceK=$2
  if ($1=="applypotential") {
    potentialcount++
    apforce[potentialcount]=$2; apforceX0[potentialcount]=$3
    }
  if ($1=="apatoms") {
    potatoms[potentialcount]=NF-1
    for (i=1;i<=potatoms[potentialcount];i++) {
      if ($(i+1)>0) apatom[potentialcount,i]=$(i+1)
      }
    }
  if ($1=="applypotentialplane") {
    appotentialplane=$2; appotentialplaneX0=$3; planeradius=$4
    }
  if ($1=="applaneatoms") {
    applaneatomnum=NF-1
    if ((appotentialplane>0) && (applaneatomnum<4)) {
      print "you need at least three atoms to define a plane"
      exit
      }
```

```
    for (i=1;i<=applaneatomnum;i++) {
      if ($(i+1)>0) applaneatoms[i]=$(i+1)
      }
    }
  blankLineTester=length($0)
  }

#get the old energy
getline < "energy"
oldenergy=$1
close("energy")

# get runpointnumber
getline < "runpointnumber"
runpointnum = $1

# get number of atoms and geometry from file testgeo
getline <  "testgeo"
numAtoms=$1
getline < "testgeo"
for (i=1;i<=numAtoms;i++) {
  getline < "testgeo"
  atSym[i]=$1
  oldarr[i,1]=$2; oldarr[i,2]=$3; oldarr[i,3]=$4
  if (atSym[i]=="H") atWeight[i]=1.00783
  if (atSym[i]=="B") atWeight[i]=10.811
  if (atSym[i]=="C") atWeight[i]=12.
  if (atSym[i]=="N") atWeight[i]=14.007
  if (atSym[i]=="O") atWeight[i]=15.9994
  if (atSym[i]=="F") atWeight[i]=18.9984
  if (atSym[i]=="Cl") atWeight[i]=35.4527
  }
}

#pull out the potential energy
/SCF Done/ || /EUMP2 =/ || / Energy=/ || /ONIOM:/ {
  if (($1=="Energy=") && ($3=="NIter="))  newPotentialE=$2
  if ($1=="SCF") newPotentialE=$5
  if ($2=="extrapolated")  newPotentialE=$5
  if ($1=="E2") {
    tempstring=$6
    split(tempstring, arr10, "D")
    newPotentialE=arr10[1]*(10^arr10[2])
    }
  newPotEK=(newPotentialE)*627.509
  }

END {
```

```
#Now we have to add in an energy based on the testgeo and the various biasing potentials
#First, we work with a sphere
if (sphereon==1) {
  biasE=0;totalweight=0
  for (i=1;i<=numAtoms;i++) {
    distToOrig=((oldarr[i,1]^2+oldarr[i,2]^2+oldarr[i,3]^2)^.5)
    if (distToOrig>spheresize) {
      biasE=biasE+0.5*sphereforceK*(distToOrig-spheresize)^2
      }
    if (distToOrig<0.9*spheresize) {
      totalweight=totalweight+atWeight[i]
      }
    }
  density=(totalweight/avNum)/((4/3)*pi*(0.9*spheresize*1E-8)^3)
  print "density",density,"sphere biasing energy",biasE >> "vellist"
  newPotEK=newPotEK+biasE
  }

#Now work on zeroatom bias
if (zeroatomon==1) {

newPotEK=newPotEK+0.5*zeroatomforceK*(oldarr[zeroatom,1]^2+oldarr[zeroatom,2]^2+olda
rr[zeroatom,3]^2)
  }

#Next, specific biasing potentials between atoms
for (k=1;k<=potentialcount;k++) {
  if ((apforce[k]!=0) && (apatom[k,1]>0) && (apatom[k,2]>0)) {
#first figure out which atom is closest to apatom[1] and put it into apatom[2]
    for (i=3;i<=potatoms[k];i++) {
      if(Distance(apatom[k,1],apatom[k,i])<Distance(apatom[k,1],apatom[k,2]))
apatom[k,2]=apatom[k,i]
      }
#now add an energy to the molecule based on the biasing potential
    biasE=0.5*apforce[k]*(Distance(apatom[k,1],apatom[k,2])-apforceX0[k])^2
    newPotEK=newPotEK+biasE
    }
  }

#routine for adding a potential based on an atoms distance from a plane defined by other atoms.
The plane should have
#a limited radius so we should really consider it as a disk
if (appotentialplane>0) {
#first figure out the center of the plane atoms and move all of the atoms to put that center at the
origin
  for (i=2;i<=applaneatomnum;i++) {
    k=applaneatoms[i]
```

```
cmass[1]=cmass[1]+oldarr[k,1];cmass[2]=cmass[2]+oldarr[k,2];cmass[3]=cmass[3]+oldarr[k,3];
    }
  numplaneatoms=applaneatomnum-1

cmass[1]=cmass[1]/numplaneatoms;cmass[2]=cmass[2]/numplaneatoms;cmass[3]=cmass[3]/nu
mplaneatoms
  for (i=1;i<=applaneatomnum;i++) {
    k=applaneatoms[i]
    newarr[k,1]=oldarr[k,1]-cmass[1];newarr[k,2]=oldarr[k,2]-
cmass[2];newarr[k,3]=oldarr[k,3]-cmass[3];
    }
#expect that bugs in process arise when plane is nearly vertical.  To avoid this, want to pick the z
dimension as the one
#that has the smallest range.  since plane is centered, can use sum of absolute values as surrogate
for range
  for (i=2;i<=applaneatomnum;i++) {
    k=applaneatoms[i]
    for (m=1;m<=3;m++) {
      if (newarr[k,m]>0) sum[m]=sum[m]+newarr[k,m];if (newarr[k,m]<0) sum[m]=sum[m]-
newarr[k,m]
      }
    }
  if (sum[1]<sum[3]) {
    for (i=1;i<=applaneatomnum;i++) {
      k=applaneatoms[i]
      tempvar=newarr[k,1];newarr[k,1]=newarr[k,3];newarr[k,3]=tempvar
      }
    tempvar=sum[1];sum[1]=sum[3];sum[3]=tempvar
    }
  if (sum[2]<sum[3]) {
    for (i=1;i<=applaneatomnum;i++) {
      k=applaneatoms[i]
      tempvar=newarr[k,2];newarr[k,2]=newarr[k,3];newarr[k,3]=tempvar
      }
    tempvar=sum[2];sum[2]=sum[3];sum[3]=tempvar
    }
#now lets find the best plane
  for (i=2;i<=applaneatomnum;i++) {
    k=applaneatoms[i]

A[1,1]=A[1,1]+newarr[k,1]^2;A[1,2]=A[1,2]+newarr[k,1]*newarr[k,2];A[1,3]=A[1,3]+newarr[k
,1]

A[2,1]=A[2,1]+newarr[k,1]*newarr[k,2];A[2,2]=A[2,2]+newarr[k,2]^2;A[2,3]=A[2,3]+newarr[k
,2]
    A[3,1]=A[3,1]+newarr[k,1];A[3,2]=A[3,2]+newarr[k,2]

b[1]=b[1]+newarr[k,1]*newarr[k,3];b[2]=b[2]+newarr[k,2]*newarr[k,3];b[3]=b[3]+newarr[k,3]
```

```
    }
  A[3,3]=numplaneatoms
  Det=A[1,1]*A[2,2]*A[3,3]+A[1,2]*A[2,3]*A[3,1]+A[1,3]*A[2,1]*A[3,2]-
A[1,3]*A[2,2]*A[3,1]-A[1,2]*A[2,1]*A[3,3]-A[1,1]*A[2,3]*A[3,2]
  E=(b[1]*A[2,2]*A[3,3]+A[1,2]*A[2,3]*b[3]+A[1,3]*b[2]*A[3,2]-A[1,3]*A[2,2]*b[3]-
A[1,2]*b[2]*A[3,3]-b[1]*A[2,3]*A[3,2])/Det
  F=(A[1,1]*b[2]*A[3,3]+b[1]*A[2,3]*A[3,1]+A[1,3]*A[2,1]*b[3]-A[1,3]*b[2]*A[3,1]-
b[1]*A[2,1]*A[3,3]-A[1,1]*A[2,3]*b[3])/Det
  G=(A[1,1]*A[2,2]*b[3]+A[1,2]*b[2]*A[3,1]+b[1]*A[2,1]*A[3,2]-b[1]*A[2,2]*A[3,1]-
A[1,2]*A[2,1]*b[3]-A[1,1]*b[2]*A[3,2])/Det
#  E, F, and G are the coefficients in the plane z=Ex+Fy+G - if the zeroing of the plane has
worked G = 0
  print "E, F, and G are the coefficients in the plane z=Ex+Fy+G",E,F,G >> "diagnostics"
  conatom=applaneatoms[1]
  distplane=(-newarr[conatom,1]*E-newarr[conatom,2]*F+newarr[conatom,3]-
G)/(E^2+F^2+1)^.5
  if (distplane<0) distplane=-distplane
  t=(newarr[conatom,1]*E+newarr[conatom,2]*F-newarr[conatom,3]+G)/(E^2+F^2+1)
  planepoint[1]=newarr[conatom,1]-t*E;planepoint[2]=newarr[conatom,2]-
t*F;planepoint[3]=newarr[conatom,3]+t
  distcmass=((planepoint[1])^2+(planepoint[2])^2+(planepoint[3])^2)^.5
  print
"distplane",distplane,"t",t,"planepoint",planepoint[1],planepoint[2],planepoint[3],"distcmass",dis
tcmass  >> "diagnostics"
  if (distcmass>planeradius) {
    planepoint[1]=(planeradius/distcmass)*planepoint[1];
    planepoint[2]=(planeradius/distcmass)*planepoint[2];
    planepoint[3]=(planeradius/distcmass)*planepoint[3];
    distcmass=((planepoint[1])^2+(planepoint[2])^2+(planepoint[3])^2)^.5
    distplane=((planepoint[1]-newarr[conatom,1])^2+(planepoint[2]-
newarr[conatom,2])^2+(planepoint[3]-newarr[conatom,3])^2)^.5
    print                                                                                    "new
distplane",distplane,"newplanepoint",planepoint[1],planepoint[2],planepoint[3],"newdistcmass",
distcmass >> "diagnostics"
    }
#finally add an energy to the molecule based on the biasing potential and distance from plane
    biasE=0.5*appotentialplane*(distplane-appotentialplaneX0)^2
    print "biasE from plane potential",biasE >> "diagnostics"
    newPotEK=newPotEK+biasE

  }

#now we decide whether or not to accept the new geometry
printon=0
if (newPotEK<oldenergy) printon=1
Ediff=newPotEK-oldenergy
if (Ediff>10) Ediff=10
if (Ediff<-10) Ediff=-10
```

```
AcceptProb=exp(-(Ediff)/(0.001987*temp))
randtest=rand()
if (randtest<AcceptProb) printon=1
printf("%i    %s %.4f %s %.4f %s %.5f %s %.6f          %i",runpointnum,"oldE",oldenergy,"new
total E",newPotEK,"AcceptProb",AcceptProb,"randomNum",randtest,printon) >> "testlist"
print "" >> "testlist"
#print                              runpointnum,"oldenergy",oldenergy,"new                              total
energy",newPotEK,"AcceptProb",AcceptProb,"randomNum",randtest,"      ",printon >> "testlist"
if (printon==1) {
  printf("%.5f",newPotEK) > "goodenergy"
  print "" >> "goodenergy"
  }
}


function Distance(Atom1,Atom2) {
 return                                    sqrt((oldarr[Atom1,1]-oldarr[Atom2,1])^2+(oldarr[Atom1,2]-
oldarr[Atom2,2])^2+(oldarr[Atom1,3]-oldarr[Atom2,3])^2)
}
```

Program proganal

```
BEGIN {
firsttitle=1
getline < "isomernumber"
isomer=$1
# read progdyn.conf for information on the plane potential atoms, if present
blankLineTester=10
while (blankLineTester>1) {
  getline < "progmc.conf"
  if ($1=="applypotentialplane") {
    appotentialplane=$2; appotentialplaneX0=$3; planeradius=$4
    }
  if ($1=="applaneatoms") {
    applaneatomnum=NF-1
    for (i=1;i<=applaneatomnum;i++) {
      if ($(i+1)>0) applaneatoms[i]=$(i+1)
      }
    }
  blankLineTester=length($0)
  }

}
/ NO2/ {
  if (firsttitle==1) {
    printf("%s %s %s %s %s %s %s  ",$1,$2,$3,$4,$6,$7,$8)
    runpoint=$6
    }
  firsttitle++
```

```
  }
/Input orientation/,/Stoichiometry/ {
  if (($1>.5) && ($1<99) && ($3=="0")) {
    A[$1]=$4;B[$1]=$5;C[$1]=$6
    i=$1
    oldarr[i,1]=$4; oldarr[i,2]=$5; oldarr[i,3]=$6
    }
  }
#/before annihilation/ {
#   printf("%s %.5f ",$1,$6)
#   }

END {
  para=Distance(1,16)
  meta=Distance(2,16)
  if (Distance(6,16)<meta) meta=Distance(6,16)
  ortho=Distance(3,16)
  if (Distance(5,16)<ortho) ortho=Distance(5,16)
  ipso=Distance(4,16)
  Opara=Distance(1,17)
  if (Distance(1,18)<Opara) Opara=Distance(1,18)
  Ometa=Distance(2,17)
  if (Distance(2,18)<Ometa) Ometa=Distance(2,18)
  if (Distance(6,17)<Ometa) Ometa=Distance(6,17)
  if (Distance(6,18)<Ometa) Ometa=Distance(6,18)
  Oortho=Distance(3,17)
  if (Distance(3,18)<Oortho) Oortho=Distance(3,18)
  if (Distance(5,17)<Oortho) Oortho=Distance(5,17)
  if (Distance(5,18)<Oortho) Oortho=Distance(5,18)
  Oipso=Distance(4,17)
  if (Distance(4,18)<Oipso) Oipso=Distance(4,18)
  NitF=Distance(16,19)
  if (Distance(16,21)<NitF) NitF=Distance(16,21)
  if (Distance(16,22)<NitF) NitF=Distance(16,22)
  if (Distance(16,23)<NitF) NitF=Distance(16,23)
  NtoPlane=Planedist(16,1,3,5,2,4,6)
  if (appotentialplane>0) NtoPlane=Planedist2()
  BC=Distance(1,20)
  if (Distance(2,20)<BC) BC=Distance(2,20)
  if (Distance(3,20)<BC) BC=Distance(3,20)
  if (Distance(4,20)<BC) BC=Distance(4,20)
  if (Distance(5,20)<BC) BC=Distance(5,20)
  if (Distance(6,20)<BC) BC=Distance(6,20)
  choice=0
  if ((Opara<Ometa) && (Opara<Oortho) && (Opara<NitF)) choice=1
  if ((Ometa<Opara) && (Ometa<Oortho) && (Ometa<NitF)) choice=2
  if ((Oortho<Ometa) && (Oortho<Opara) && (Oortho<NitF)) choice=3
  if (Ometa<2) choice=2
```

```
  if (Oortho<2) choice=3
  if (choice==0) printf("%s %.3f %s %.3f %s %.3f %s %.3f %s %.3f %s %.2f
","p",para,"m",meta,"o",ortho,"i",ipso,"NtoPlane",NtoPlane,"BC",BC)
  if (choice==1) printf("%s %.3f %s %.3f %s %.3f %s %.3f %s %.3f %s %.2f
","p",para,"m",meta,"o",ortho,"i",ipso,"NtoPlane",NtoPlane,"BC",BC)
  if (choice==2) printf("%s %.3f %s %.3f %s %.3f %s %.3f %s %.3f %s %.2f
","p",para,"m",meta,"o",ortho,"i",ipso,"NtoPlane",NtoPlane,"BC",BC)
  if (choice==3) printf("%s %.3f %s %.3f %s %.3f %s %.3f %s %.3f %s %.2f
","p",para,"m",meta,"o",ortho,"i",ipso,"NtoPlane",NtoPlane,"BC",BC)
  if (runpoint>500000) {
    print "Too many points.  XXXXN"
#    system("date > nogo")
    }
  if (para<1.6) {
#    print "para product formed XXXX"
#    system("date > nogo")
    }
  if (meta<1.6) {
#    print "meta product formed XXXX"
#    system("date > nogo")
    }
  if (ortho<1.6) {
#    print "ortho product formed XXXX"
#    system("date > nogo")
    }
  if (ipso<1.6) {
#    print "ipso product formed XXXX"
#    system("date > nogo")
    }
  if (Opara<1.6) {
#    print "Opara product formed XXXX"
    }
  if (Ometa<1.6) {
#    print "Ometa product formed XXXX"
    }
  if (Oortho<1.6) {
#    print "Oortho product formed XXXX"
    }
  if (Oipso<1.6) {
#    print "Oipso product formed XXXX"
    }
#  if (NitF<1.6) {
#    print "NitF product formed XXXX"
#    system("date > nogo")
#    }
  if ((para>5) && (meta>5) && (ortho>5)) {
#    if ((para<5.2) || (para>5.25)) print "Dissociated to SM XXXX"
    }
```

```
  system("date '+%b:%d:%Y %T'")
  }

function Distance(Atom1,Atom2) {
 return sqrt((A[Atom1]-A[Atom2])^2 + (B[Atom1]-B[Atom2])^2 + (C[Atom1]-C[Atom2])^2)
}

function Angle(Atom1,Atom2,Atom3) {
  value=((-
Distance(Atom1,Atom3)^2+Distance(Atom1,Atom2)^2+Distance(Atom2,Atom3)^2)/(2*Distanc
e(Atom1,Atom2)*Distance(Atom2,Atom3)))
  return acos(value)
}

function Planedist2() {
#first figure out the center of the plane atoms and move all of the atoms to put that center at the
origin
  cmass[1]=0;cmass[2]=0;cmass[3]=0
  for (i=2;i<=applaneatomnum;i++) {
    k=applaneatoms[i]

cmass[1]=cmass[1]+oldarr[k,1];cmass[2]=cmass[2]+oldarr[k,2];cmass[3]=cmass[3]+oldarr[k,3];
    }
  numplaneatoms=applaneatomnum-1

cmass[1]=cmass[1]/numplaneatoms;cmass[2]=cmass[2]/numplaneatoms;cmass[3]=cmass[3]/nu
mplaneatoms
#  print "center of masse",cmass[1],cmass[2],cmass[3]
  for (i=1;i<=applaneatomnum;i++) {
    k=applaneatoms[i]
#    print k,oldarr[k,1],oldarr[k,2],oldarr[k,3]
    newarr[k,1]=oldarr[k,1]-cmass[1];newarr[k,2]=oldarr[k,2]-
cmass[2];newarr[k,3]=oldarr[k,3]-cmass[3];
#    print "            new",k,newarr[k,1],newarr[k,2],newarr[k,3]
    }
#expect that bugs in process arise when plane is nearly vertical.  To avoid this, want to pick the z
dimension as the one
#that has the smallest range.  since plane is centered, can use sum of absolute values as surrogate
for range
  for (i=2;i<=applaneatomnum;i++) {
    k=applaneatoms[i]
    for (m=1;m<=3;m++) {
      if (newarr[k,m]>0) sum[m]=sum[m]+newarr[k,m];if (newarr[k,m]<0) sum[m]=sum[m]-
newarr[k,m]
      }
    }
  if (sum[1]<sum[3]) {
```

```
    for (i=1;i<=applaneatomnum;i++) {
      k=applaneatoms[i]
      tempvar=newarr[k,1];newarr[k,1]=newarr[k,3];newarr[k,3]=tempvar
      }
    tempvar=sum[1];sum[1]=sum[3];sum[3]=tempvar
    }
  if (sum[2]<sum[3]) {
    for (i=1;i<=applaneatomnum;i++) {
      k=applaneatoms[i]
      tempvar=newarr[k,2];newarr[k,2]=newarr[k,3];newarr[k,3]=tempvar
      }
    tempvar=sum[2];sum[2]=sum[3];sum[3]=tempvar
    }
#now lets find the best plane

A[1,1]=0;A[1,2]=0;A[1,3]=0;A[2,1]=0;A[2,2]=0;A[2,3]=0;A[3,1]=0;A[3,2]=0;A[3,3]=0;b[1]=0;
b[2]=0;b[3]=0
  for (i=2;i<=applaneatomnum;i++) {
    k=applaneatoms[i]

A[1,1]=A[1,1]+newarr[k,1]^2;A[1,2]=A[1,2]+newarr[k,1]*newarr[k,2];A[1,3]=A[1,3]+newarr[k
,1]

A[2,1]=A[2,1]+newarr[k,1]*newarr[k,2];A[2,2]=A[2,2]+newarr[k,2]^2;A[2,3]=A[2,3]+newarr[k
,2]
    A[3,1]=A[3,1]+newarr[k,1];A[3,2]=A[3,2]+newarr[k,2]

b[1]=b[1]+newarr[k,1]*newarr[k,3];b[2]=b[2]+newarr[k,2]*newarr[k,3];b[3]=b[3]+newarr[k,3]
    }
  A[3,3]=numplaneatoms
  Det=A[1,1]*A[2,2]*A[3,3]+A[1,2]*A[2,3]*A[3,1]+A[1,3]*A[2,1]*A[3,2]-
A[1,3]*A[2,2]*A[3,1]-A[1,2]*A[2,1]*A[3,3]-A[1,1]*A[2,3]*A[3,2]
  E=(b[1]*A[2,2]*A[3,3]+A[1,2]*A[2,3]*b[3]+A[1,3]*b[2]*A[3,2]-A[1,3]*A[2,2]*b[3]-
A[1,2]*b[2]*A[3,3]-b[1]*A[2,3]*A[3,2])/Det
  F=(A[1,1]*b[2]*A[3,3]+b[1]*A[2,3]*A[3,1]+A[1,3]*A[2,1]*b[3]-A[1,3]*b[2]*A[3,1]-
b[1]*A[2,1]*A[3,3]-A[1,1]*A[2,3]*b[3])/Det
  G=(A[1,1]*A[2,2]*b[3]+A[1,2]*b[2]*A[3,1]+b[1]*A[2,1]*A[3,2]-b[1]*A[2,2]*A[3,1]-
A[1,2]*A[2,1]*b[3]-A[1,1]*b[2]*A[3,2])/Det
#  E, F, and G are the coefficients in the plane z=Ex+Fy+G - if the zeroing of the plane has
worked G = 0
#  print "E, F, and G are the coefficients in the plane z=Ex+Fy+G",E,F,G
  conatom=applaneatoms[1]
  distplane=(-newarr[conatom,1]*E-newarr[conatom,2]*F+newarr[conatom,3]-
G)/(E^2+F^2+1)^.5
  if (distplane<0) distplane=-distplane
  t=(newarr[conatom,1]*E+newarr[conatom,2]*F-newarr[conatom,3]+G)/(E^2+F^2+1)
  planepoint[1]=newarr[conatom,1]-t*E;planepoint[2]=newarr[conatom,2]-
t*F;planepoint[3]=newarr[conatom,3]+t
```

```
  distcmass=((planepoint[1])^2+(planepoint[2])^2+(planepoint[3])^2)^.5
#                                                
```

```
A[1,2]*A[2,1]*b[3]-A[1,1]*b[2]*A[3,2])/Det
#  E, F, and G are the coefficients in the plane z=Ex+Fy+G"
# make a function that tests the fit
  for (i=2;i<8;i++) {
    if (afplaneatoms[i]>.5) {
      k=afplaneatoms[i]
      distplane=(-A[k]*E-B[k]*F+C[k]-G)/(E^2+F^2+1)^.5;if (distplane<0) distplane=-distplane
      aberror=aberror+distplane
      }
    }
# if the fit is bad, as can happen, decrease to 3 atoms in plane, using only the first three atoms in
list after the conatom
  if (aberror>2) {
    print "proganal original aberror",aberror >> "diagnostics"
    A[1,1]=0;A[1,2]=0;A[1,3]=0;A[2,1]=0;A[2,2]=0;A[2,3]=0;A[3,1]=0;A[3,2]=0;A[3,3]=0
    for (i=2;i<5;i++) {
      k=afplaneatoms[i]
      A[1,1]=A[1,1]+A[k]^2;A[1,2]=A[1,2]+A[k]*B[k];A[1,3]=A[1,3]+A[k]
      A[2,1]=A[2,1]+A[k]*B[k];A[2,2]=A[2,2]+B[k]^2;A[2,3]=A[2,3]+B[k]
      A[3,1]=A[3,1]+A[k];A[3,2]=A[3,2]+B[k];A[3,3]++
      b[1]=b[1]+A[k]*C[k];b[2]=b[2]+B[k]*C[k];b[3]=b[3]+C[k]
      }
    Det=A[1,1]*A[2,2]*A[3,3]+A[1,2]*A[2,3]*A[3,1]+A[1,3]*A[2,1]*A[3,2]-
A[1,3]*A[2,2]*A[3,1]-A[1,2]*A[2,1]*A[3,3]-A[1,1]*A[2,3]*A[3,2]
    E=(b[1]*A[2,2]*A[3,3]+A[1,2]*A[2,3]*b[3]+A[1,3]*b[2]*A[3,2]-A[1,3]*A[2,2]*b[3]-
A[1,2]*b[2]*A[3,3]-b[1]*A[2,3]*A[3,2])/Det
    F=(A[1,1]*b[2]*A[3,3]+b[1]*A[2,3]*A[3,1]+A[1,3]*A[2,1]*b[3]-A[1,3]*b[2]*A[3,1]-
b[1]*A[2,1]*A[3,3]-A[1,1]*A[2,3]*b[3])/Det
    G=(A[1,1]*A[2,2]*b[3]+A[1,2]*b[2]*A[3,1]+b[1]*A[2,1]*A[3,2]-b[1]*A[2,2]*A[3,1]-
A[1,2]*A[2,1]*b[3]-A[1,1]*b[2]*A[3,2])/Det
    aberror=0
    for (i=2;i<5;i++) {
      k=afplaneatoms[i]
      distplane=(-A[k]*E-B[k]*F+C[k]-G)/(E^2+F^2+1)^.5;if (distplane<0) distplane=-distplane
      aberror=aberror+distplane
      }
    }
  if (aberror>2) {
#     printf("%s %.2f ","aberror",aberror)
     return 99999999
    }
  conatom=afplaneatoms[1]
  distplane=(-A[conatom]*E-B[conatom]*F+C[conatom]-G)/(E^2+F^2+1)^.5
  if (distplane<0) distplane=-distplane
  t=(A[conatom]*E+B[conatom]*F-C[conatom]+G)/(E^2+F^2+1)
  planepoint[1]=A[conatom]-t*E;planepoint[2]=B[conatom]-t*F;planepoint[3]=C[conatom]+t
  distcmass=((planepoint[1]-cmass[1])^2+(planepoint[2]-cmass[2])^2+(planepoint[3]-
cmass[3])^2)^.5
```

```
  if (distcmass>1.4) {
    vector[1]=planepoint[1]-cmass[1];vector[2]=planepoint[2]-
cmass[2];vector[3]=planepoint[3]-cmass[3]

vector[1]=vector[1]*1.4/distcmass;vector[2]=vector[2]*1.4/distcmass;vector[3]=vector[3]*1.4/di
stcmass

planepoint[1]=cmass[1]+vector[1];planepoint[2]=cmass[2]+vector[2];planepoint[3]=cmass[3]+v
ector[3];
    distcmass=((planepoint[1]-cmass[1])^2+(planepoint[2]-cmass[2])^2+(planepoint[3]-
cmass[3])^2)^.5
    distplane=((planepoint[1]-A[conatom])^2+(planepoint[2]-B[conatom])^2+(planepoint[3]-
C[conatom])^2)^.5
#                                                                    print "new
distplane",distplane,"newplanepoint",planepoint[1],planepoint[2],planepoint[3],"newdistcmass",
distcmass >> "diagnostics"
    }

  return distplane
  }

function asin(x) { return (180/3.141592)*atan2(x, sqrt(1-x*x)) }

function acos(x) { return (180/3.141592)*atan2(sqrt(1-x*x), x) }

function atan(x) { return (180/3.141592)*atan2(x,1) }

function Dihedral(Atom1,Atom2,Atom3,Atom4) {
  B1x=A[Atom2]-A[Atom1]
  B1y=B[Atom2]-B[Atom1]
  B1z=C[Atom2]-C[Atom1]
  B2x=A[Atom3]-A[Atom2]
  B2y=B[Atom3]-B[Atom2]
  B2z=C[Atom3]-C[Atom2]
  B3x=A[Atom4]-A[Atom3]
  B3y=B[Atom4]-B[Atom3]
  B3z=C[Atom4]-C[Atom3]
  modB2=sqrt((B2x^2)+(B2y^2)+(B2z^2))
# yAx is x-coord. etc of modulus of B2 times B1
  yAx=modB2*(B1x)
  yAy=modB2*(B1y)
  yAz=modB2*(B1z)
# CP2 is the crossproduct of B2 and B3
  CP2x=(B2y*B3z)-(B2z*B3y)
  CP2y=(B2z*B3x)-(B2x*B3z)
  CP2z=(B2x*B3y)-(B2y*B3x)
  termY=((yAx*CP2x)+(yAy*CP2y)+(yAz*CP2z))
# CP is the crossproduct of B1 and B2
```

```
  CPx=(B1y*B2z)-(B1z*B2y)
  CPy=(B1z*B2x)-(B1x*B2z)
  CPz=(B1x*B2y)-(B1y*B2x)
  termX=((CPx*CP2x)+(CPy*CP2y)+(CPz*CP2z))
 dihed4=(180/3.141592)*atan2(termY,termX)
 return dihed4
}

function killdyn(isomer) {
  system("rm -f dyn")
}
```

Program progmc.conf

```
#This is the configuration file for PROGMC.  This file is read by progMC and
# the awk programs progmcb and progEcheck
#The programs won't read anything past the first blank line,
#and this file must end with a blank line.
#Do not delete lines - rather, comment out lines for unwanted options.
#The values here are read repeatedly and most can be changed in the middle of running jobs
#***The keywords are case sensitive.  The following keywords should always be defined:***
#***method, charge, multiplicity, memory, processors, title
#*** method --The following word is copied exactly to the gaussian input file.
method ONIOM(M062X/6-311G*:PM3)
#*** method2 --The options here are restricted, unrestricted, and read. restricted is the default
#If the method is U..., put unrestricted here and the .com files will have in them guess=mix.
#If you put read here, the .com files will contain guess=tcheck, which sometimes makes things
faster, sometimes not.
#The use of read requires a specifically defined checkpoint file name using the keyword
checkpoint.
method2 read
charge 0
multiplicity 1
oniomchargemult 1 1
processors 3
#*** memory --The following "word" is copied exactly to the gaussian input file after %mem=.
memory 7gb
#*** killcheck and checkpoint -- You can use a specifically defined checkpoint file name by
putting
#the name after the keyword checkpoint.  This is necessary if you use the read option with
method2.
#Defined checkpoint names are an unnecessary modest hastle and if you do not want to bother,
use killcheck 0
killcheck 0
checkpoint g09.chk
#*** diagnostics -- 0 prints out nothing extra, 1 (default) prints out extra stuff to a
#file "diagnostics"
diagnostics 0
#*** title -- the title keyword must be followed by exactly four words
```

```
title NO2+Tol 101CH2Cl2IonP Oniom MonteCarlo
temperature 298.15
#SPECIFIC MONTE CARLO OPTIONS ****
#*** mcstepsize sets the maximum distance in each dimension that atoms can be moved for each new point and is applied to all atoms
mcstepsize 0.0010
lengthstep 0.001
anglestep 0.005
#mcmolrotangle sets the maximum angle in degrees for rotation of molecules about X, Y, Z axes through molecule center of mass
mcmolrotangle 1.00
# molecule specifications - divides system into molecules and allows a separate stepsize for each molecule.  This is in addition to the step above.
molecule 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 0.02
molecule 16 17 18 0.02
molecule 19 20 21 22 23 0.02
molecule 24 25 26 27 28 0.02
molecule 29 30 31 32 33 0.02
molecule 34 35 36 37 38 0.02
molecule 39 40 41 42 43 0.02
molecule 44 45 46 47 48 0.02
molecule 49 50 51 52 53 0.02
molecule 54 55 56 57 58 0.02
molecule 59 60 61 62 63 0.02
molecule 64 65 66 67 68 0.02
molecule 69 70 71 72 73 0.02
molecule 74 75 76 77 78 0.02
molecule 79 80 81 82 83 0.02
molecule 84 85 86 87 88 0.02
molecule 89 90 91 92 93 0.02
molecule 94 95 96 97 98 0.02
molecule 99 100 101 102 103 0.02
molecule 104 105 106 107 108 0.02
molecule 109 110 111 112 113 0.02
molecule 114 115 116 117 118 0.02
molecule 119 120 121 122 123 0.02
molecule 124 125 126 127 128 0.02
molecule 129 130 131 132 133 0.02
molecule 134 135 136 137 138 0.02
molecule 139 140 141 142 143 0.02
molecule 144 145 146 147 148 0.02
molecule 149 150 151 152 153 0.02
molecule 154 155 156 157 158 0.02
molecule 159 160 161 162 163 0.02
molecule 164 165 166 167 168 0.02
molecule 169 170 171 172 173 0.02
molecule 174 175 176 177 178 0.02
molecule 179 180 181 182 183 0.02
```

molecule 184 185 186 187 188 0.02
molecule 189 190 191 192 193 0.02
molecule 194 195 196 197 198 0.02
molecule 199 200 201 202 203 0.02
molecule 204 205 206 207 208 0.02
molecule 209 210 211 212 213 0.02
molecule 214 215 216 217 218 0.02
molecule 219 220 221 222 223 0.02
molecule 224 225 226 227 228 0.02
molecule 229 230 231 232 233 0.02
molecule 234 235 236 237 238 0.02
molecule 239 240 241 242 243 0.02
molecule 244 245 246 247 248 0.02
molecule 249 250 251 252 253 0.02
molecule 254 255 256 257 258 0.02
molecule 259 260 261 262 263 0.02
molecule 264 265 266 267 268 0.02
molecule 269 270 271 272 273 0.02
molecule 274 275 276 277 278 0.02
molecule 279 280 281 282 283 0.02
molecule 284 285 286 287 288 0.02
molecule 289 290 291 292 293 0.02
molecule 294 295 296 297 298 0.02
molecule 299 300 301 302 303 0.02
molecule 304 305 306 307 308 0.02
molecule 309 310 311 312 313 0.02
molecule 314 315 316 317 318 0.02
molecule 319 320 321 322 323 0.02
molecule 324 325 326 327 328 0.02
molecule 329 330 331 332 333 0.02
molecule 334 335 336 337 338 0.02
molecule 339 340 341 342 343 0.02
molecule 344 345 346 347 348 0.02
molecule 349 350 351 352 353 0.02
molecule 354 355 356 357 358 0.02
molecule 359 360 361 362 363 0.02
molecule 364 365 366 367 368 0.02
molecule 369 370 371 372 373 0.02
molecule 374 375 376 377 378 0.02
molecule 379 380 381 382 383 0.02
molecule 384 385 386 387 388 0.02
molecule 389 390 391 392 393 0.02
molecule 394 395 396 397 398 0.02
molecule 399 400 401 402 403 0.02
molecule 404 405 406 407 408 0.02
molecule 409 410 411 412 413 0.02
molecule 414 415 416 417 418 0.02
molecule 419 420 421 422 423 0.02

molecule 424 425 426 427 428 0.02
molecule 429 430 431 432 433 0.02
molecule 434 435 436 437 438 0.02
molecule 439 440 441 442 443 0.02
molecule 444 445 446 447 448 0.02
molecule 449 450 451 452 453 0.02
molecule 454 455 456 457 458 0.02
molecule 459 460 461 462 463 0.02
molecule 464 465 466 467 468 0.02
molecule 469 470 471 472 473 0.02
molecule 474 475 476 477 478 0.02
molecule 479 480 481 482 483 0.02
molecule 484 485 486 487 488 0.02
molecule 489 490 491 492 493 0.02
molecule 494 495 496 497 498 0.02
molecule 499 500 501 502 503 0.02
molecule 504 505 506 507 508 0.02
molecule 509 510 511 512 513 0.02
molecule 514 515 516 517 518 0.02
molecule 519 520 521 522 523 0.02
molecule 524 525 526 527 528 0.02
#*** method3, method4, method5, and method6 -- These keywords let you add extra lines to the gaussian input file.
#method3 and method4 add lines at the top of the input after the lines defining the method, and
#this is useful to implement things like the iop for mPW1k
#method5 and method6 add lines after the geometry, after a blank line of course
#only a single term with no spaces can be added, one per method line. Here are some examples to uncomment if needed
#method3 IOp(3/76=0572004280)
method3 scf=(conver=5)
#method3 scrf=(pcm,Solvent=dichloromethane)
#add the line below with big structures to get it to put out the distance matrix and the input orientation
method4 iop(2/9=2000)
#method4 iop(3/124=3)
#method4 scrf=(pcm,solvent=dmso,read)
#method5 radii=bondi
#method6
#*** methodfile -- This keyword lets you add more complicated endings to gaussian input files
#such as a gen basis set. Put after the keyword the number of lines in a file you create called
#methodfile that contains the test you want to add to the end of the gaussian input
methodfile 0
#*** highlevel --For ONIOM jobs, the following line states the number of highlevel atoms,
#which must come before the medium level atoms. Use some high value such as 999 if not using ONIOM
highlevel 18
#applypotential adds energy to bias the MC. Format is applypotential forceConstant(E=.5k(x-x0)^2) x0

#the force constant is in kcal/mol/ang^2
#apatoms choses the atoms with format apatoms firstatom secondatom [additional atoms]
applypotential 118.56 2.35
apatoms 16 1 2 3 4 5 6
#applypotentialplane sets a energy addition to constrain an atom to a distance from a plane defined by other atoms.
#if the number of atoms defining the plane is >3, the plane is a
#least squares best fit keyword applaneatoms is followed first by the atom being set and then by the series of atoms, up to 6, that define the plane
#first number is forceConstant kcal/mol/ang^2, second is distance in angstroms
#applypotentialplane 100 2.1
#applaneatoms 16 1 3 5 2 4 6
#zeroatom pushes the numbered atom toward the origin with a harmonic potential set by second number in kcal/mol/ang^2
zeroatom 16 1
#*** boxon and boxsize - With boxon 1, a cubic box is set such that atoms that reach the edge
#are reflected back toward the middle. Useful for dynamics with solvent molecules. This is a crude
#implementation that is ok for a few thousand femtoseconds but will not conserve energy long term.
#Set the box size so as to fit the entire initial molecule but not have too much extra room.
#The dimensions of the box are two times the boxsize, e.g. boxsize 7.5 leads to a box that is 15 x 15 x 15 angstroms
#boxon 1
#boxsize 11.2
#*** sphereon and spheresize and sphereforce - uses a force to push atoms within a sphere. notice that if the atom is far outside of
#the sphere then the force is large unless sphereforce is set small
sphereon 1
spheresize 12.9
sphereforce 11.85

#created Dec 21, 2015

Program whamnitmc

```
cd ~
rm -f ~/regiocount
rm -f n1??/seriesfile*
awk -v pt=3000 -f ~/progseriesmc n16?/mcfollowfile > n160/seriesfile
awk -v pt=3000 -f ~/progseriesmc n154/mcfollowfile n155/mcfollowfile n156/mcfollowfile n157/mcfollowfile n158/mcfollowfile n159/mcfollowfile > n154/seriesfile
awk -v pt=4000 -f ~/progseriesmc n112/mcfollowfile n142/mcfollowfile n143/mcfollowfile n144/mcfollowfile n145/mcfollowfile> n112/seriesfile
awk -f ~/progseriesmc n106/mcfollowfile n107/mcfollowfile n108/mcfollowfile n109/mcfollowfile n110/mcfollowfile n111/mcfollowfile > n106/seriesfile
awk -f ~/progseriesmc n100/mcfollowfile n101/mcfollowfile n102/mcfollowfile n103/mcfollowfile n104/mcfollowfile n105/mcfollowfile > n100/seriesfile
awk -f ~/progseriesmc n113/mcfollowfile n114/mcfollowfile > n113/seriesfile
```

```
awk -f ~/progseriesmc n115//mcfollowfile n146/mcfollowfile > n115/seriesfile
awk -f ~/progseriesmc n116/mcfollowfile n117/mcfollowfile n118/mcfollowfile > n116/seriesfile
awk -f ~/progseriesmc n119/mcfollowfile n120/mcfollowfile > n119/seriesfile
awk -f ~/progseriesmc n121/mcfollowfile n122/mcfollowfile > n121/seriesfile
awk -f ~/progseriesmc n123/mcfollowfile n124/mcfollowfile > n123/seriesfile
awk -f ~/progseriesmc n125/mcfollowfile n126/mcfollowfile > n125/seriesfile
awk -f ~/progseriesmc n127/mcfollowfile n128/mcfollowfile > n127/seriesfile
awk -f ~/progseriesmc n129/mcfollowfile n147/mcfollowfile > n129/seriesfile
cd ~/wham/wham
./wham 1.475 5.675 84 0.000001 298.15 0 metadatafile.nitrationmc ~/output.nitrationfull 6 23
cd
cat output.nitrationfull
cat ~/regiocount
cat ~/wham/wham/metadatafile.nitrationmc
```

Program progseriesmc

```
BEGIN {
if (pt<1) startfile=100
if (pt>1) startfile=pt
countpara=0;countmeta=0;countortho=0;countipso=0;counttotal=0
oldfilename=""
switches=-1
current="";oldclosest=""
currentop=""
oldop=""
opswitches=-1
}
/NO2/ {
if (oldfilename!=FILENAME) {
  if (counttotal>0) {
    pp=int(.5+100*countpara/counttotal)
    pm=int(.5+100*countmeta/counttotal)
    po=int(.5+100*countortho/counttotal)
    pi=int(.5+100*countipso/counttotal)
    print oldfilename," ",countpara,countmeta,countortho,countipso," ",counttotal," ",pp,pm,po,pi," switches",switches," opswitches",opswitches >> "regiocount"
    }
  if (counttotal==0) print "" >> "regiocount"
  countpara=0;countmeta=0;countortho=0;countipso=0;counttotal=0;switches=-1;current="";oldclosest="";opswitches=-1;oldop=""
  fileline=0
  }
oldfilename=FILENAME
fileline++
if (fileline>startfile) {
  counttotal++
  if (($7<$9) && ($7<$11) && ($7<$13)) {
```

```
    countpara++
    current="para"
    currentop="para"
    }
  if (($9<$7) && ($9<$11) && ($9<$13)) {
    countmeta++
    current="meta"
    }
  if (($11<$7) && ($11<$9) && ($11<$13)) {
    countortho++
    current="ortho"
    currentop="ortho"
    }
  if (($13<$7) && ($13<$9) && ($13<$11)) {
    countipso++
    current="ipso"
    }
  if (current!=oldclosest) switches++
  if (currentop!=oldop) opswitches++
  oldclosest=current; oldop=currentop
  dist=$7
  if ($9<dist) dist=$9
  if ($11<dist) dist=$11
  if ($13<dist) dist=$13
  printf("%.1f %.3f",$5,dist)
  print ""
  }
}
END {
if (counttotal>0) {
  pp=int(.5+100*countpara/counttotal)
  pm=int(.5+100*countmeta/counttotal)
  po=int(.5+100*countortho/counttotal)
  pi=int(.5+100*countipso/counttotal)
  }
print  oldfilename,"              ",countpara,countmeta,countortho,countipso,"            ",counttotal,"
",pp,pm,po,pi,"     switches",switches,"  opswitches",opswitches >> "regiocount"
}
```